THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

STRUCTURE AND STABILITY OF HEAD-TO-HEAD PVC

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PREFACE

The work described in this thesis was carried out during the period October 1971 to September 1974 at the University of Glasgow in the Department of Physical Chemistry, which is under the supervision of Professor G.A. Sim.

I am indebted primarily to the Science Research Council for the award of a Research Studentship and to my supervisor Dr. I.C. McNeill, for his advice and constant encouragement.

Finally, I would like to thank Messrs. J. Gorman and R. Ferrie for their technical assistance and all members of the Polymer Group for their tolerance and good humour.

S U M M A R Y

STRUCTURE AND STABILITY OF HEAD-TO-HEAD PVC

Most addition polymers are thought to be formed by head-to-tail addition of monomer units. Previous studies of PVC have confirmed that the structure is head-to-tail, although the possible presence of a small number of head-to-head units cannot be discounted. It has been suggested that it is these head-to-head structures which are responsible for the relative instability of PVC compared to model compounds. By chlorination of polybutadiene under carefully controlled conditions, a model PVC has been obtained which is made up entirely of head-to-head units

A comprehensive study of the thermal degradation of this model head-to-head PVC has been carried out using mainly the techniques of thermal volatilisation analysis, which involves programmed heating up to 500^{0}C. under vacuum conditions, and thermogravimetry under a dynamic nitrogen atmosphere. Degradation occurs by hydrogen chloride elimination which commences well below 200^{0} but does not cease till 400^{0}. Over 95% of the available chlorine is lost as hydrogen chloride, which accounts for all of the material lost in the main stage of breakdown. Above 400^{0} small amounts of ethylene and propylene are detected, while the involatile residue of degradation shows strong similarities to that obtained in degradation of normal PVC. Conjugation was found to be extensive in the partially-degraded polymer, with long polyene sequences being present very early in

the degradation.

As a means of gaining additional insight into the mechanism of dehydrochlorination, the degradation of poly(methyl methacrylate)/head-to-head PVC blends has been studied; the behaviour has been compared with that previously found for PVC/PMMA blends. PMMA is initially less stable and gives monomer at temperatures corresponding to dehydrochlorination of head-to-head PVC. The interaction is explained in terms of attack on PMMA by chlorine atoms from the degrading head-to-head PVC

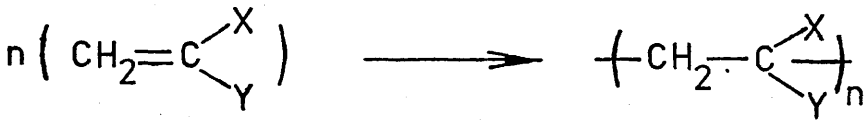
The kinetics of degradation have been studied under programmed and isothermal conditions by thermal volatilisation analysis and thermogravimetry. Values of reaction order and activation energy have been obtained which are consistent with a radical chain process. Although both kinetic and blend studies suggest a radical chain process, the formation of polyene sequences cannot readily be explained by this mechanism. It is concluded that more than one type of mechanism is in operation.

C O N T E N T S

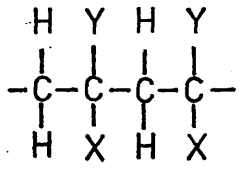
CHAPTER ONE

INTRODUCTION

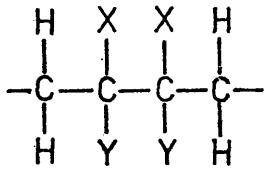
Polymeric materials can be regarded as long chains or networks built up from simple units derived from the monomer. For a monomer of the vinyl type this may be represented as follows :



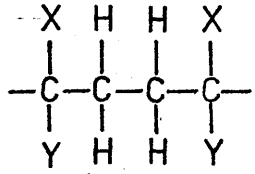
If the methylene group is considered to be the tail of a monomer unit and the carbon atom containing X and Y the head, it is possible to describe the connecting monomer units as head-to-tail, head-to-head, or tail-to-tail structures.



HEAD-TO-TAIL



HEAD-TO-HEAD

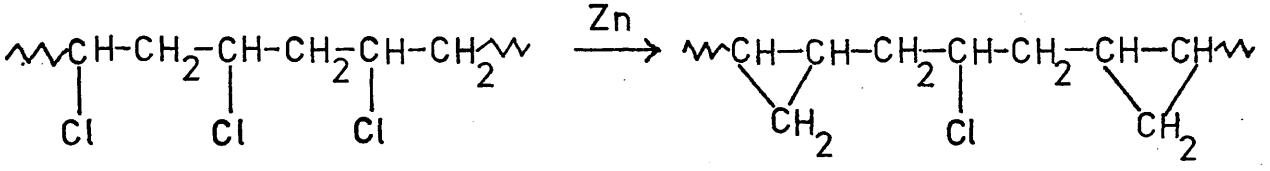


TAIL-TO-TAIL

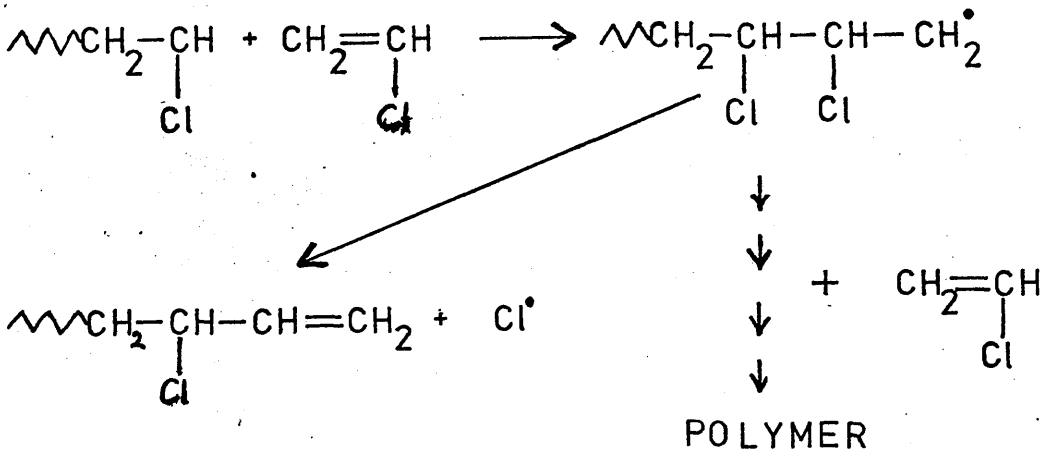
There is little reason to doubt that polymers in general are constructed preponderantly by head-to-tail addition. Historically, poly(vinyl chloride) was one of the first polymers for which direct evidence of head-to-tail addition was obtained [1,2]. However, the

accuracy of the method used hardly precludes the possibility of a minor amount of vicinal dichloride structures formed by head-to-head addition or 1,4 dichlorides formed by tail-to-tail addition.

The experiment employed to establish the sequential distribution of chlorine atoms was based on a proposal by Flory [2], that if random coupling of substituents can be effected with polymers having the 1,3 -structure, occasionally single substituents will be left between neighbours which have reacted. On a statistical basis 13.53% will be left unreacted in a 1,3 structure while in a random structure residual content will be 18.4%. Marvel, Sample and Roy[1] demonstrated this by reacting zinc dust with PVC in a dioxan solution. Experimental values obtained showed that 13-16% of chlorine was retained, which corresponds closely to a head-to-tail structure.

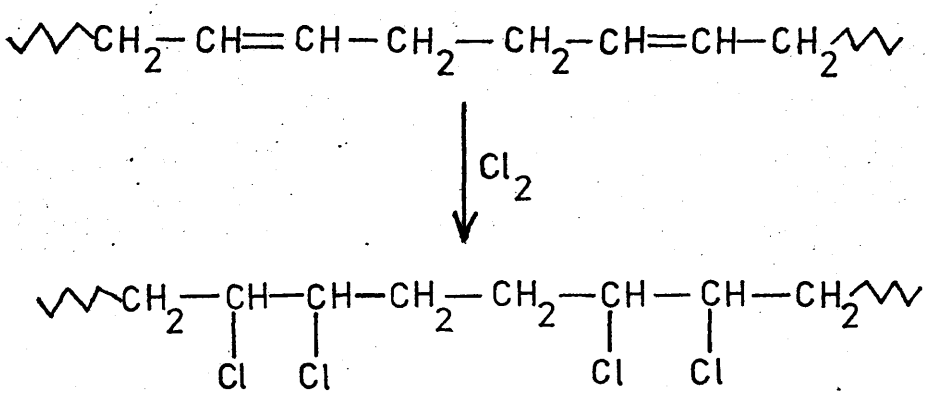


However, the results do not preclude a certain amount of head-to-head structure. More recently, in the case of the polymerisation of vinyl chloride, the lack of dependence of the molecular weight on initiator concentration has been ascribed to reactions of the following sort occurring during polymerisation[3].



In general the evidence for head-to-head structures in poly (vinyl chloride) is meagre, although Ohtsu[4] and Nakata have reported evidence suggesting 1.5 mole per cent head-to-head units, while Wilson[5] and co-workers have shown that poly(vinyl fluoride) contains as many as 1 in 6 head-to-head units. Nevertheless the presence of head-to-head structures is thought to be one of the reasons for the relative instability of poly(vinyl chloride) compared with model compounds. (A fuller discussion will be given in Chapter 4.)

A knowledge of the behaviour of a model head-to-head poly(vinyl chloride) would shed light therefore on the relative importance of head-to-head structures in poly(vinyl chloride). Model head-to-head poly(vinyl chloride) can be prepared by the straightforward addition chlorination of polybutadiene which is shown overleaf.



However, the reaction conditions must be carefully controlled[6] or substitution reactions may also occur and a model head-to-head PVC compound will not be obtained. This reaction is discussed fully in Chapter 3. The chlorination of polybutadiene has been investigated by many workers[7-10]. However, degradation experiments are limited to two sources.

Firstly, Amagi and co-workers[11] have obtained a simple thermogravimetric curve for the model head-to-head PVC compound, and by comparing this with a curve obtained for head-to-tail PVC they made some speculative proposals regarding its mechanism of degradation.

Secondly, Ito and co-workers[12] have subjected the model polymer to pyrolysis gas chromatography and from analysis of the products confirmed the structure of the polymer. Therefore, apart from some tentative proposals [11] no real evidence has been produced which can classify the mechanism of degradation as being radical, ionic or unimolecular in nature.

POLYMER DEGRADATION

Due to the increasing importance of polymers as commercial products, a large amount of research work has been done to investigate how these polymers behave in a particular environment, or under the influence of a particular agency such as heat, light, radiation or mechanical stress. The term "degradation" implies any chemical modification in the polymer. Chemical modification is generally associated with a deterioration in the physical properties which make the polymer useful commercially.

Degradation can be brought about by a variety of agencies, e.g. heat, ultraviolet light, high energy radiation, mechanical stress. However, fundamental studies are usually restricted to reactions initiated by a single agency in order that the number of variables in the system may be minimised. Experimentally, thermal degradation is one of the easiest to study since all that is required is a heat source and an accurate measurement of the temperature of the polymer sample.

In an atmosphere of oxygen, energy supplied to the polymer may result in the formation of hydroperoxides in the chain, and hence to more rapid degradation. In order to remove these complicating oxidative effects degradation is often studied in vacuum or under a stream of inert gas.

In the work described in this thesis, heat was the only agency used so that further discussion is limited to thermal degradation.

THE REASONS FOR STUDYING THERMAL DEGRADATION

Thermal degradation studies have been used extensively to examine the breakdown pattern of polymers and hence provide useful information regarding their stability and effectiveness as commerical materials.

In addition, thermal degradation studies have become increasingly important as a means of characterising macromolecular structure. By a careful study particularly of the products of degradation, detailed information can be obtained concerning the sequence and arrangement of monomer units in the backbone, as well as the nature and importance of cross-links and chain-end groups.

CLASSIFICATION OF DEGRADATION REACTIONS

Two types of degradation reaction can be distinguished in the thermal breakdown of polymers :

(a) Chain scission reactions.

(b) Substituent reactions.

Chain scission reactions are those in which the basic structure of the polymer chain remains unaltered. Degradation occurs by rupture of the main backbone of the polymer chain. The products from this type of degradation are similar in structure to the parent material, containing both monomer units and longer chain fragments.

Substituent reactions are those in which the basic structure of the polymer chain is altered. The chemical nature of the repeat unit is changed by modification of structural groups or total elimination of substituents. Products from this type of degradation are unlike monomer in chemical structure.

(A) CHAIN SCISSION REACTIONS

These are generally free-radical in nature. Scission of the chain to form free radicals occurs at chain ends or at random along the backbone. Two types of reaction may now occur. Monomer may be produced by a simple reverse polymerisation process known as depropagation, or higher chain fragments may result when transfer reactions occur between polymer chains.

Simha, Wall and Blatz[13-16], have shown that their reactions may be summarised by a mechanism of the following general type :

Random initiation $M_n \xrightarrow{k_i} P_j + P_{n-j}$

Chain-end initiation $M_n \xrightarrow{k_i} P_{n-1} + M_1$

Depropagation $P_i \xrightarrow{k_d} P_{i-1} + M_1$

Transfer $P_i + M_n \xrightarrow{k_f} M_i + P_n$ intermolecular

$P_n \longrightarrow P_j + M_{n-j}$ intramolecular

Termination $P_i + P_j \xrightarrow{k_t} M_i + M_j$ or M_{i+j}

In these equations n = chain length of starting material , P_i and P_j etc. M_i, M_j etc. represent respectively long chain radicals and dead polymer molecules of i, j etc. monomer units in length. It

has also been shown that the competing processes of depropagation and transfer are responsible for the distinct degradation patterns in different polymers. Poly(methyl methacrylate)[17] and Poly (α-methyl styrene)[18] are examples where depropagation is the main process occurring. High monomer yields are produced with both of these polymers while molecular weight remains constant since only whole molecules are being removed.

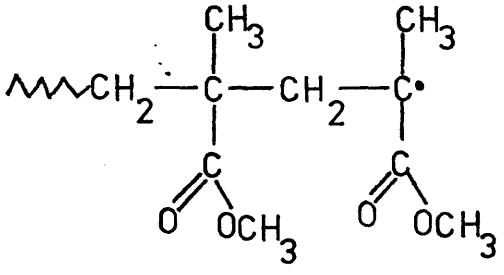
Polyethylene is an example where molecular transfer is the predominant reaction. Transfer is either inter-molecular or intramolecular depending on whether the polyethylene is linear or branched[19]. Monomer yield is very low and a wide range of chain fragments is produced. Molecular weight changes however, depend on the relative amounts of inter and intramolecular transfer involved. Most polymers which degrade by a chain scission process show a degradation pattern in which appreciable amounts of both monomer and higher chain fragments are involved.

Hence the degradation pattern of a particular polymer often lies somewhere between the extreme examples mentioned above. However, careful studies of molecular weight changes (or rate of degradation as a function of molecular weight), products of degradation and monomer yields, help to give a useful qualitative picture of the degradation mechanism with respect to the relative importance of transfer and depropagation reactions.

EFFECT OF POLYMER STRUCTURE ON CHAIN SCISSION MECHANISM

Although a careful study of the type described overleaf will give information on the relative importance of transfer and depropagation reactions, it is often possible to predict which type of process will predominate by a detailed study of the polymer structure. The reactivity of a polymer radical and the presence of reactive atoms are factors which influence the degradation process. Hence by examining a polymer for reactive hydrogen atoms, and structures which will stabilise radicals, a degradation mechanism can often be predicted.

Polystyrene is an example of a polymer which exhibits both types of behaviour during degradation, [18]. The polymer radicals are readily stabilised due to the close proximity of the benzene rings, however these radicals may also abstract the reactive hydrogens from another polymer chain. PMMA is a polymer which shows a 100% depropagation process during degradation [17]. This can be easily explained if we examine that basic structure of PMMA:



The polymer radical produced during PMMA degradation is unreactive due to delocalisation of the free electron into the adjacent carbonyl group. Stability is also enhanced by the high degree

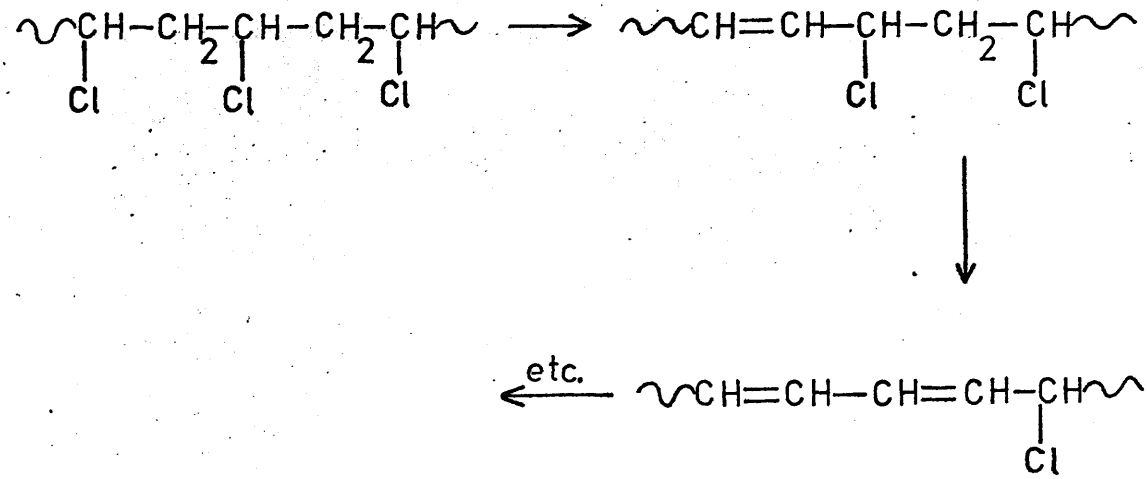
of substitution of the radical, while the hydrogens are protected from attack by the steric hindrance of bulky neighbouring groups. Hence degradation will be by depropagation only. This can be compared with poly (styrene). Although the radicals are stabilised by resonance, the hydrogen atoms are less sterically hindered and hence abstraction is a competing reaction.

(B) SUBSTITUENT REACTIONS

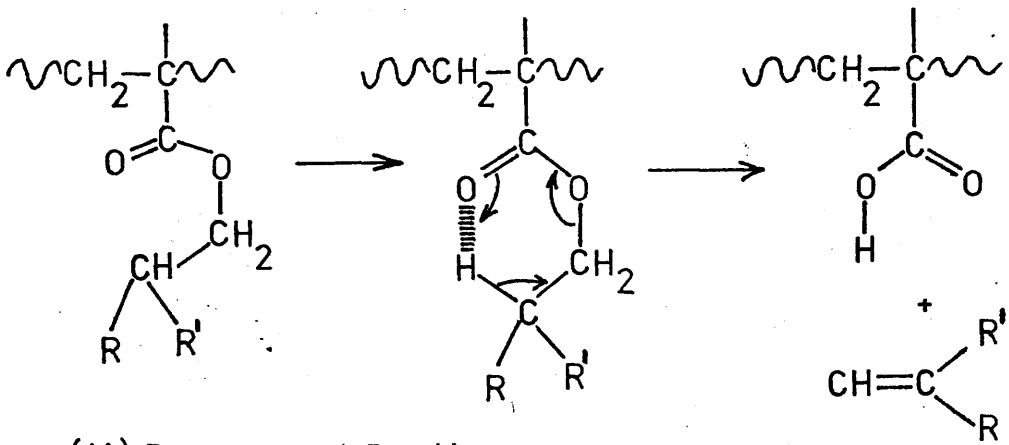
These differ from chain scission reactions in that processes occurring may be either free radical, ionic or molecular in nature. The mechanism of degradation depends mainly on the chemical nature of the functional groups. Substituent reactions can only assume any significance when degradation temperature is lower than that required for rupture of the main polymer backbone. Substituent reactions can be subdivided into two main types.

(i) Elimination Reactions.

These involve the removal of small molecules from the polymer with subsequent change in the backbone. This type of reaction is very common in the case of the thermal degradation of chlorine containing polymers. Chlorine is eliminated from the polymers as hydrogen chloride and double bonds are formed along the backbone. Poly(vinyl chloride)[20] is a good example of this type of reaction. Hydrogen chloride is liberated from adjacent units, producing conjugated double bonds.

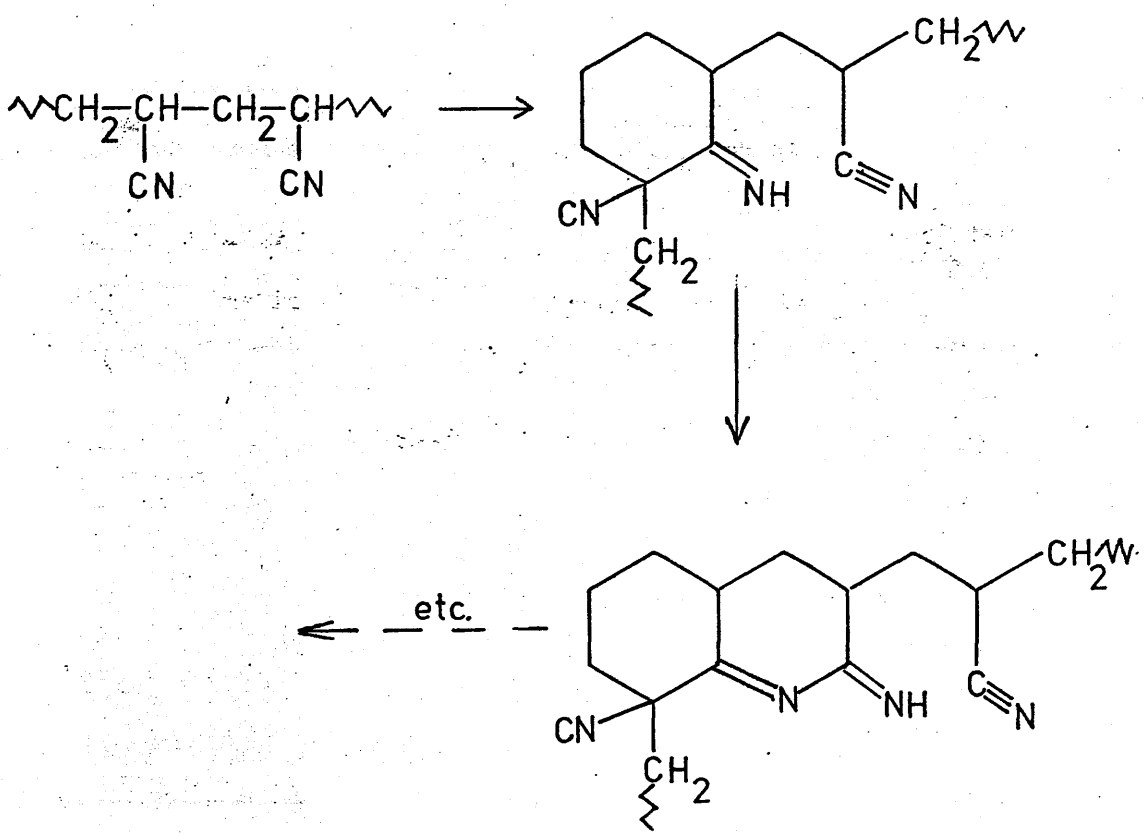


This reaction will be discussed in greater depth in Chapter 4. Elimination reactions during degradation are also characteristic of a number of polyvinyl esters. Poly (vinyl acetate) [21] eliminates acetic acid on heating, to produce a conjugated polymer backbone. This type of reaction is also shown by some of the higher methacrylates.

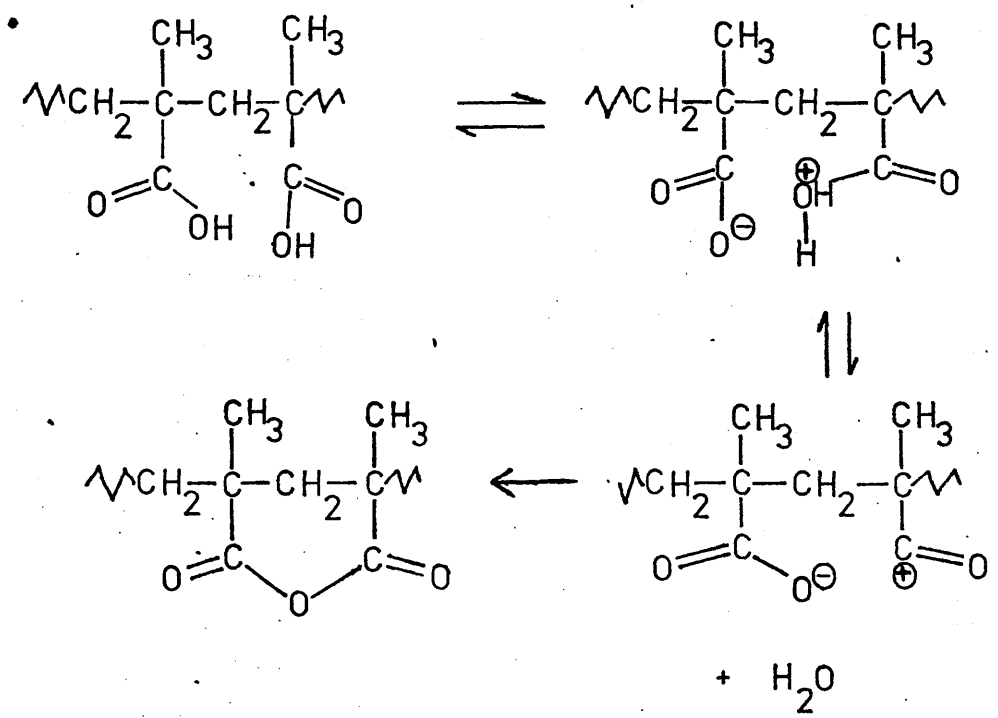


(ii) Rearrangement Reactions

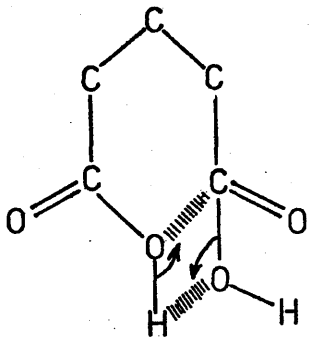
These involve alteration of the basic unit of the polymer chain by intramolecular rearrangements, sometimes associated with elimination. Poly(acrylonitrile)[22,23] is a good example of this type of reaction. The following rearrangement occurs in the early stages of degradation giving rise to colouration.



The degradation of poly(methacrylic acid) [24] is a reaction in which both elimination and rearrangment processes are occurring.

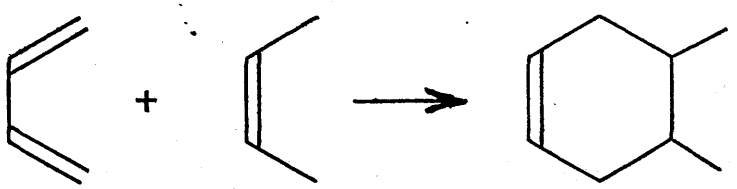


Elimination involves the removal of a water molecule while the rearrangement occurs through the intermediate species shown below:



CROSS-LINKING REACTIONS

In these reactions polymer chains are joined together to form a three dimensional network. This often leads to insolubility and a characteristic rise in the molecular weight of the polymer. Cross-links are thought to be formed either by combination of pairs of radicals so that the phenomenon may constitute the termination step in a degradation process, or by reaction of unsaturated carbon atoms in a Diels-Alder type process.



AIM OF PRESENT STUDIES

The motivation for studying chlorinated polybutadiene was two-fold. First it was desirable to make a detailed study of the chlorination of polybutadiene under vacuum conditions and compare the results with those of previous workers who studied this reaction under a wide variety of reaction conditions.

More emphasis, however, was placed upon an extensive investigation into the thermal degradation of chlorinated polybutadiene. It was anticipated that the degradation would prove to be interesting due to the similarity in structure to PVC. In addition since head-to-head units are thought to play some part in the degradation of PVC it was hoped that a detailed study of chlorinated polybutadiene (corresponding to head-to-head PVC) would shed light not only on its own mechanism of degradation, but also on that of PVC. Particular attention was paid to the dehydrochlorination and kinetic parameters were sought by several different methods. The reason for this is that differences in mechanism are often reflected in very different values of activation energy. In the degradation of chlorinated polybutadiene, an important structural feature appears to forbid the production of hydrogen chloride by an analogous mechanism to that for PVC.

The dehydrochlorination of PVC goes by a stepwise process and depends on allylic activation of a neighbouring chlorine atom.

It will be shown that in head-to-head PVC no chlorine atom is available in an "activated" allylic position, hence the degradation might be expected to be markedly different from that of head-to-tail PVC. It is therefore of interest to observe whether the model head-to-head PVC does in fact degrade by a different mechanism. The degradation behaviour of head -to-head PVC is studied fully in Chapter 4. However, it was considered important to review the degradation behaviour of head-to-tail PVC prior to studying the degradation of head-to-head PVC and this is done fully in the introduction to Chapter 4.

Chapter 5 is devoted to the study of blend systems of head-to-head PVC with various polymers to try to obtain further information which may be useful in formulating a degradation mechanism, while Chapter 6 is devoted to the study of the corresponding bromine polymer ; head-to-head PVBr.

CHAPTER TWO

EXPERIMENTAL TECHNIQUES

THERMAL VOLATILISATION ANALYSIS (TVA)

TVA is now a well established technique of thermal analysis and has been described by McNeill previously [25,26]. However, since TVA was used as a primary means of characterising polymer degradation, it is convenient to give a brief description.

PRINCIPLE OF TVA

When a sample is heated in a continuously evacuated system, a pressure develops as degradation occurs and the volatile products of degradation distil from the hot sample zone to a cold trap. Pirani gauges which are situated between the sample tube and the cold trap measure this pressure.

A thermogram is produced recording Pirani output as a function of temperature. A diagram of this basic TVA system is shown in Fig. 1. The heating arrangement consists of a Perkin Elmer F11 oven with linear temperature programmer, which can heat the sample isothermally, or from ambient temperatures, up to 500°C using linear rates of heating ranging from 1° to 40° per minute. Details of the oven assembly are given in Fig. 2. The temperature of the oven is measured by a chromel-alumel thermocouple fixed just below the base of the degradation tube. The degradation tube is approximately 6" long and is constructed from a Pyrex FG35 flange, with a pyrex glass base. The top of the tube and the greased flange joint are cooled by a

Fig. 1

BASIC TVA APPARATUS

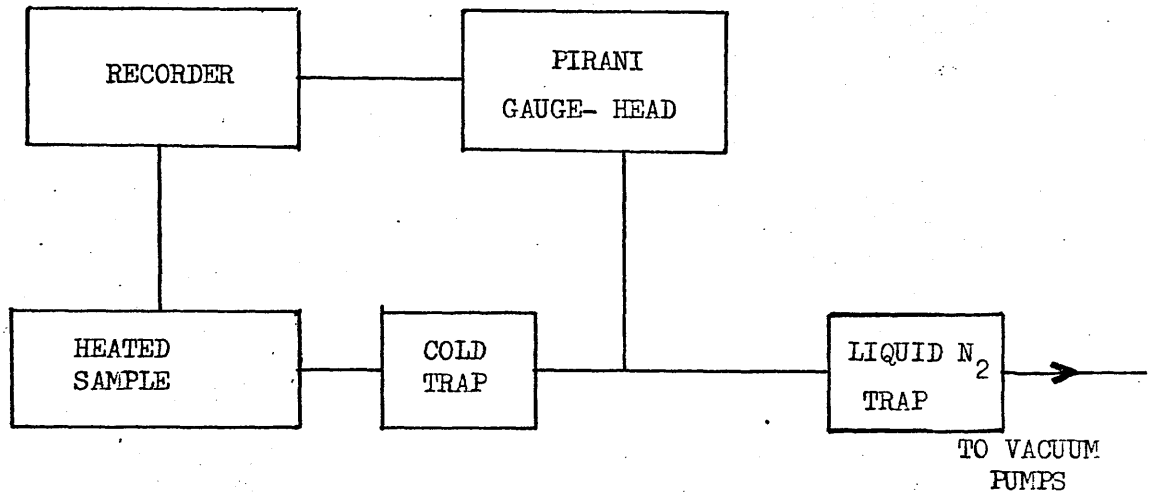
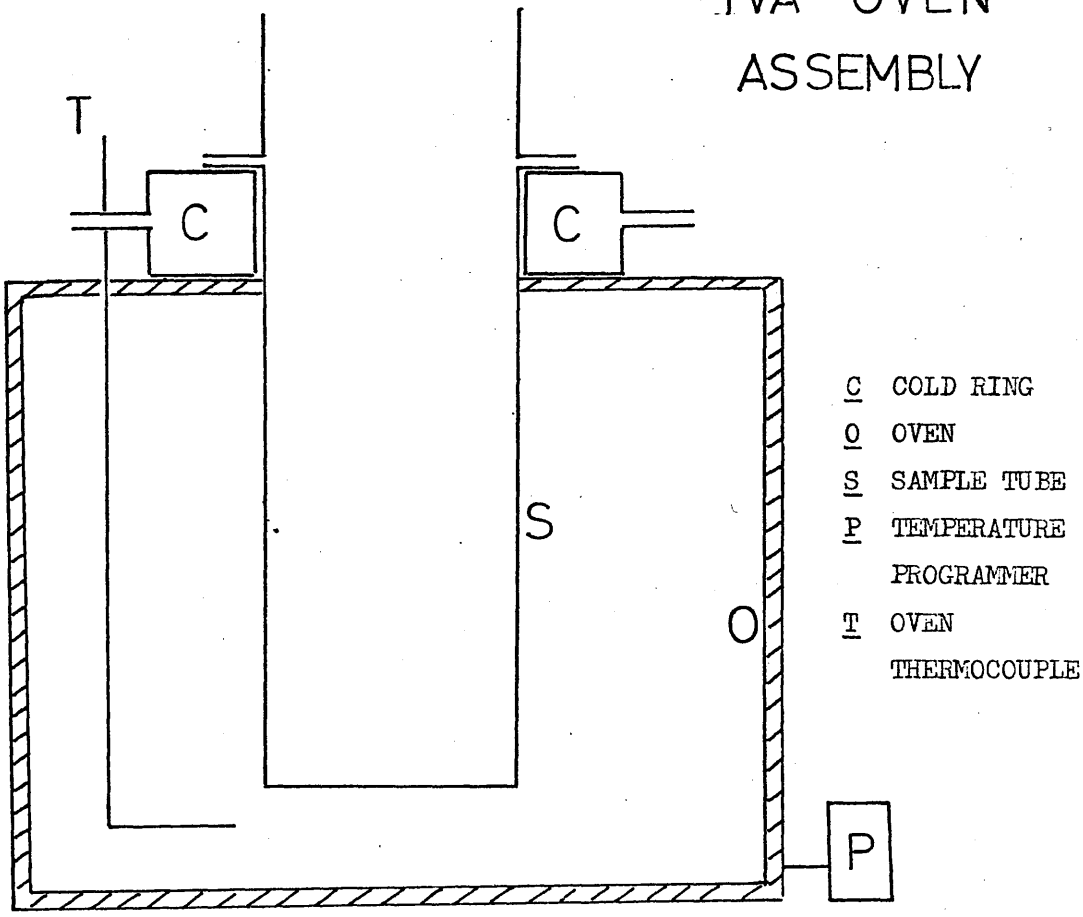


Fig. 2

TVA OVEN ASSEMBLY



water jacket.

DIFFERENTIAL CONDENSATION TVA

In the simple TVA apparatus, products may be classified by whether or not they are condensable in liquid nitrogen. This principle of differential condensability may be extended by the use of other traps at different temperatures as described by McNeill [27]. A schematic diagram of the apparatus is shown in Fig. 3. The volatile products of degradation are pumped along four equivalent routes to a liquid nitrogen trap. Each route contains a secondary trap operating at a different temperature, 0°, -45°, -75° and -100° respectively. A Pirani gauge is positioned after each trap including the liquid nitrogen trap. The Pirani responses are transmitted via a multi gauge head unit, to a twelve channel recorder where they are recorded simultaneously with the oven temperature and a differential condensation TVA thermogram is thus obtained.

TEMPERATURE CALIBRATION

The temperature reading obtained during degradation is measured by the oven thermocouple. This is lower than the actual sample temperature since there is a thermal gradient across the base of the degradation tube. This temperature lag, which is a function of heating rate, sample temperature and position of thermocouple, is caused by the insulating effect of the Pyrex glass and by heat lost through the cooling-jacket. The internal temperature at the base of sample was determined as

Fig 3

DIFFERENTIAL CONDENSATION TVA ASSEMBLY

follows.

A second thermocouple was introduced into the sample tube. The junction at the point of contact between the metal and the glass was surrounded by a small amount of Apiezon "L" grease to simulate molten polymer, and to ensure good thermal contact. Oven temperature was now increased and the outputs from the oven thermocouple and the thermocouple resting on the inside base of the sample tube were recorded simultaneously. The temperature lag was plotted as a function of temperature. It was found that for increased heating rates temperature lag increased, although at higher temperatures it was found to decrease. The results also showed that for a particular heating rate thermal lag was constant over a number of runs[27].

SAMPLE HEATING RATE

All TVA data in the present work including T_{max} values (i.e. the temperature at which peak maxima occur) refer to a programmed heating rate of 10°C per minute.

By means of spectroscopic analysis of the products and a prior knowledge of the behaviour of various substances in the different traps, it is often possible to obtain a useful qualitative picture of the degradation pattern at various temperatures. When a product shows a "limiting rate" behaviour in one of the traps this often facilitates its identification. The limiting rate occurs when a product condenses in one of the initial traps, but then slowly begins to distil over into the -196°C trap. The Pirani response generated is often seen as a "plateau" and the displacement of this (in millivolts)

from the base line is often characteristic for a particular material.

PRODUCT ANALYSIS OF TVA FRACTIONS

The products of degradation fall into three categories:

(i) Volatiles

(ii) Non-Volatiles

(iii) Cold-Ring Fraction

(i) Volatiles

The volatiles are those materials which are volatile at both degradation and ambient temperature. Volatiles which are fully condensed in the liquid nitrogen trap (-196°C) in the continuously pumped system are referred to as "condensables". These may be subsequently distilled into an Infra Red gas cell attachment, Mass Spectrometer sample tube or cold finger capillary for GLC analysis. Those materials not fully condensed at -196°C in a continuously pumped system are referred to as "non-condensables". These are normally analysed by degradation in a closed system. Products from this type of degradation are collected in an Infra Red gas cell attachment or mass spectrometer sample tube with the liquid nitrogen trap in place.

(ii) Non-Volatiles

The non-volatile materials are those remaining at the base of the sample tube after degradation. They may be removed as a solid and ground with KBr. to form a disc for Infra Red analysis, or elemental analysis may be undertaken directly.

(iii) Cold-Ring Fractions

The cold ring fraction is made up of those substances which are

volatile at degradation temperature but involatile at ambient temperature. These products condense on the upper part of the degradation tube which is surrounded by a cooling jacket. A tissue moistened with a suitable solvent such as chloroform or carbon tetrachloride is used to remove this fraction from the degradation tube. Subsequent extractions from the tissue allows these products to be analysed by Infra Red spectroscopy either in solution cells or as compacted KBr discs.

THERMOGRAVIMETRY

Thermogravimetry (TG) is a well established thermal analysis technique in which the weight of a sample is continuously recorded as the temperature is raised linearly. TG curves were obtained from a Du Pont 900 Differential Thermal Analyser with accessory 950 TG module. Samples of 5-20mg were degraded in a dynamic nitrogen atmosphere.

A boat-shaped platinum sample holder was used which measured 1cm. x 0.5cm. x 0.25cm. deep. The temperature measuring thermocouple was located 0.1cm. from sample holder. Isothermal experiments were carried out using TG to study the kinetics of dehydrochlorination of polymer samples. In this case the residual weight of polymer was plotted as a function of time at a fixed temperature.

ULTRA-VIOLET (UV) SPECTROSCOPY

Because of the insolubility of the degraded polymer and because unsupported films of suitable thickness were found extremely difficult to handle, the ultra violet spectra. investigated were of films degraded on a silica glass support. TVA degradation tubes with overall length 115mm. were constructed in silica glass to fit the sample cavity of the Unicam SP800 Spectrophotometer used in this work. The light loss due to absorption and reflection by the 2mm. thick silica window forming the base of the tube was found to be only 10% and to be entirely compensated by an identical tube placed in the reference beam of the instrument.

The temperature lag was found to be about 12°C greater for the shorter tubes by comparison of the TVA curves obtained using silica and Pyrex degradation tubes. Films were cast on the base of the tube (10 sq. cm. in area) by evaporating 1ml. of a solution of the polymer in cyclohexanone in a vacuum oven at 40°C.

PROTON MAGNETIC RESONANCE SPECTROSCOPY

Proton Magnetic Resonance Spectra were used to follow the reaction of chlorine with polybutadiene. Spectra were obtained using a Jeol C60 HL High Resolution NMR Spectrometer (60 MHz). Quantitative information could be obtained from the spectra since the intensity of the signal or the area under the peak is proportional to the number of hydrogen

atoms in that environment. The ratio of the peak areas was obtained by using the integrator attached to the spectrometer. Since chloroform was a suitable solvent, the polymers were studied as solutions in deuterochloroform which has no hydrogen atom absorption .

GAS-LIQUID CHROMATOGRAPHY

Quantative data was obtained using a Perkin Elmer F11 Gas Chromatograph equipped with a hot wire analyser, or a Microtek GC2000, Research Gas Chromatograph equipped with a flame ionisation detector.

For quantitative analysis the procedure involved adding a known weight of a suitable material as internal standard to a weighed quantity of the liquid sample. Several mixtures of pure samples of each of the products were made up with known amounts of the internal standard and run on the chromatograph to determine the sensitivities of the product compounds relative to the standard. Since the peak area for a particular substance is proportional to the weight present, the peak areas on the GLC traces were measured by planimetry or by the method of weighing "cut-outs". If the sensitivity factor (f) for any product is defined as the ratio of the peak area of product to standard when equal weights of both are considered, then the percentage by weight of S in G grams of sample is given by -

$$\% S = \frac{\text{peak area of S}}{\text{peak area of standard}} \times \frac{100}{G/\text{wt. of standard}} \cdot \frac{1}{f}$$

MOLECULAR WEIGHTS

For the polymers which were soluble in toluene, the number average molecular weights were obtained from osmotic pressure measurements at 20°C. The instrument used was a Mechrolab Model 501 High Speed Osmometer with Sylvania 300 grade gel cellophane membrane.

The polymers which were insoluble in toluene were sent to the Polymer Supply and Characterisation Centre, where the molecular weight values were determined by Gel Permeation Chromatography (GPC).

INFRA RED SPECTROSCOPY

Spectra were recorded on a Perkin Elmer 257 Spectrophotometer. Polymer samples and residues were examined as films cast from solution on to NaCl plates or as compacted KBr discs. Volatile degradation products were examined using a gas cell attachment

Quantitative I.R. was used to determine the Cis/trans ratio in the sample of polybutadiene. Spectra were obtained using solution cells of known dimensions, and the method of analysis used was that of Yates and Thornton [28].

POLYMER BLENDS

INCOMPATIBILITY

Before any discussion can take place on the interactions observed in polymer blend systems, it is necessary to look at the physical state of the system since macromolecules are generally incompatible in the solid state and also under certain conditions in solution. This is easily demonstrated by dissolving different polymers in a common solvent. Above a certain limiting concentration, the solution divides into two separate layers with a distinct phase boundary between them. Each layer contains almost exclusively one of the polymers. Similar incompatibility occurs in the solid phase [29,30].

If the polymers are compatible, transparent blends are obtained, if incompatible then blends are usually opaque [31,32]. Compatibility of polymer solutions is a function of temperature [29,33]. the molecular weight of the polymers [34] concentration of the polymers in solution [35] and the chemical nature of the polymer chain [34]. Polymer blends therefore will not form a true mixture. In the solid state, domains or micelles of one polymer will be distributed throughout the matrix of the second polymer. Any chemical interaction observed therefore must occur at the phase boundary or involve the diffusion of one species into the other phase. In order to make valid comparisons, sample form must be reproducible throughout a series of experiments. This is obtained when one species is dispersed to the same

extent in the matrix of the other in every case.

COMPARISON OF MIXED AND UNMIXED SYSTEMS.

In any study of the degradation of mixed polymer systems, a method is required for comparing mixed and unmixed systems of the polymer pair under similar conditions.

One approach to this problem used by Grassie, McNeill and Cooke [36], is to obtain TVA curves for known weights of the component polymers, and for the same weights of the polymers in the form of a mixture; and then to determine whether the behaviour of the latter is consistent with what would be expected by simply "adding" the TVA curves for the individual polymers.

A more convenient technique described by McNeill and Neil [37], involving fewer experiments, was adapted. This method involved degrading known weights of the two polymers simultaneously, but in an unmixed condition, and comparing the results of those obtained using the same experimental arrangement, but with mixed samples.

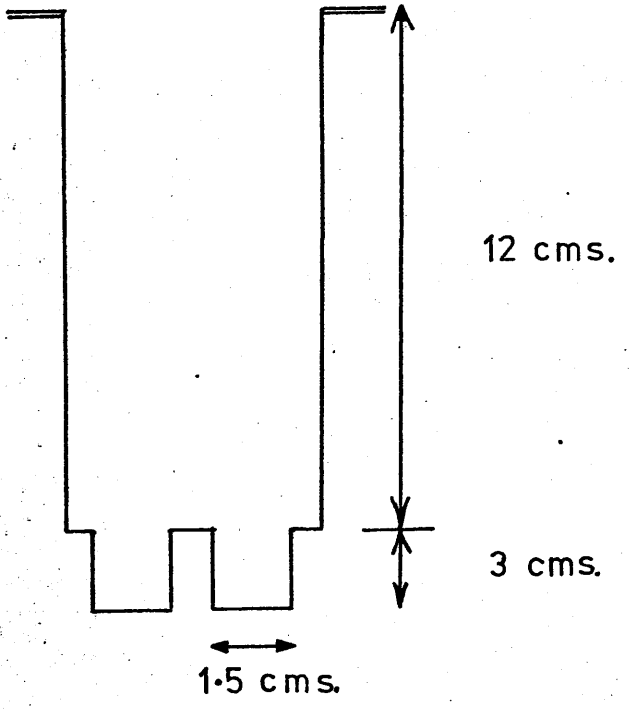
PREPARATION OF MIXED AND UNMIXED SAMPLES

Solutions of the two polymers (10mg./ml.) were made up in a common solvent. For the study of unmixed systems, equal volumes of the two solutions were placed in separate limbs of the special degradation tube, described by McNeill and Neil [37] and depicted in Fig. 4.

The solvent was removed under continuous pumping in a vacuum oven at 40°C. For the study of mixed systems, suitable volumes of

Fig.4

Twin-limbed degradation tube.



the polymer solutions were mixed thoroughly by continuous shaking. When the mixture of the polymer solutions was left to stand over a period of time, no phase separation was observed. Equal volumes of the mixture were now placed in the two limbs of the degradation tube, and the polymer films were made as before. As long as this procedure was rigorously followed the TVA curves obtained were reproducible and heterogeneity of the polymer system was assumed to be constant.

CHAPTER THREE

CHLORINATION OF POLYBUTADIENE

In order to obtain a pure head-to-head PVC polymer, chlorination of polybutadiene must proceed only by chlorine addition across the double bond. Any substitution reaction taking place would result in a different chlorinated structure, and any subsequent comparison of the supposed head-to-head structure with head-to-tail PVC would be invalid.

The addition chlorination of polybutadiene has been studied by many workers [7-10]. In general they recommend chlorination in chloroform solution in the presence of a catalyst such as ferric chloride which favours the ionic addition reaction rather than the radical substitution. However, Ita [12] and co-workers have shown that under these conditions small amounts of local substitution take place. Dall'Asta [6] and co-workers have carried out chlorinations on a whole series of poly (alkenamers) to produce a range of poly(1,2 dihaloalkamer)s in the absence of a specific catalyst and using methylene chloride as the solvent. Under these conditions, no substitution chlorination was observed.

In the work described in this chapter, chlorination experiments were carried out under vacuum using a variety of

solvent systems and also under nitrogen atmosphere and air for comparison with the work of previous authors.

PURIFICATION OF COMMERCIAL POLYBUTADIENE

The Polybutadiene used in this work was Ameripol CB221, a gift from B.H. Goodrich Company Limited. Analysis by infra red spectroscopy [28] showed that the polymer contained 98.5% cis units, 1% trans units and 0.5% vinyl units. Before use the polymer was purified by reprecipitation. Toluene was used as solvent and the polymer solution allowed to stand so that it could be decanted from the small amount of sediment at the bottom of the flask. The polymer was precipitated in methanol and re-dissolved under nitrogen.

When the polymer was completely re-dissolved, the solution was filtered and the filtrate was reprecipitated under nitrogen from dilute solution. This process was repeated once more and the resulting white elastic polybutadiene was dried under vacuum for several days during which time it was progressively cut into smaller pieces. When exposed to air, the polymer progressively yellowed, but when stored under vacuum in the dark no yellowing occurred. In order to keep oxidation effects to an absolute minimum, fresh polymer was purified before starting any set of chlorination experiments. The number average molecular weight (Mn) of the purified polymer was determined to be 40,800 by osmometry.

CHLORINATION UNDER VACUUM

The apparatus used for the chlorination of polybutadiene under vacuum conditions is shown in Fig. 5. The volume of the small reservoir Y was approximately one fifteenth of the 3 litre reservoir X. Stopcocks 1, 2, 3, 4 were greaseless (Teflon TF2/13). The reaction tubes were joined to the apparatus by means of greaseless "Viton" cone and socket joints.

At the point V a "Vacustat" gauge (Model 2G, Edwards High Vacuum Limited) was joined to the apparatus and used for checking the vacuum. At best evacuation, the pressure was of the order 10^{-5} - 10^{-6} torr, and a "sticking" vacuum was observed in the gauge. The Pirani gauge was now calibrated and the "Vacustat" gauge removed. Subsequent evacuation of the apparatus was monitored by means of the Pirani gauge.

CALIBRATION OF CHLORINATION APPARATUS

Chlorine gas was introduced into the system using the following technique. Chlorine (I.C.I. Ltd., Mond Division) was passed into a modified U-tube as shown in Fig. 6. When the vessel was filled with chlorine at atmospheric pressure, it was sealed by closing the stopcocks. The U-tube was now attached to the chlorination apparatus at the point P by means of a greaseless Viton cone and socket joint and the chlorine was distilled into the reservoir. This process was repeated until sufficient chlorine had been collected in the reservoir.

Fig. 5

CHLORINATION APPARATUS

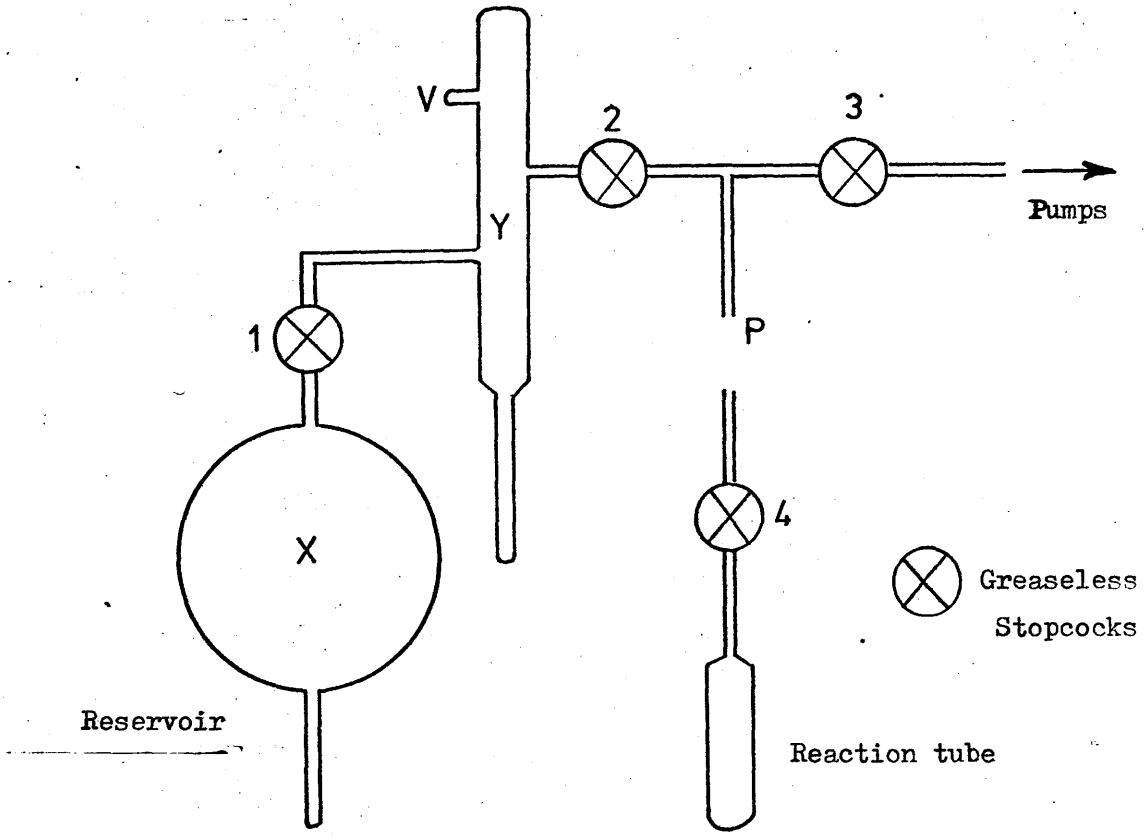
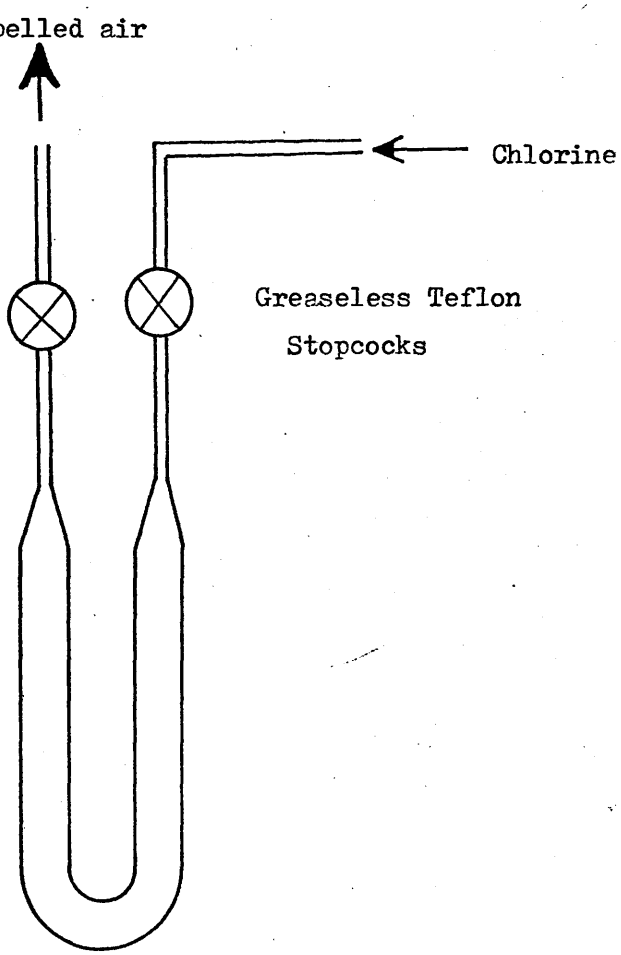


Fig. 6

Modified U-tube for chlorine transfer.



CHLORINATION OF POLYBUTADIENE

Solutions of polybutadiene were made up in methylene chloride, chloroform and carbon tetrachloride. The solutions were transferred to reaction tubes and attached to the chlorination apparatus at the point P. The polymer solutions were frozen in liquid nitrogen, evacuated and allowed to thaw.

This process was repeated three times until degassing of the solutions was complete. The degree of evacuation and degassing was followed using a Pirani pressure gauge. When degassing was complete a suitable amount of chlorine was distilled from the reservoir into the reaction vessel as previously described. The vessel was then sealed off and removed from the line. The reaction was thus allowed to proceed in the evacuated tube and will subsequently be referred to as "reaction under vacuum ".

PURIFICATION OF CHLORINATED POLYBUTADIENE

Chlorination of polybutadiene was generally carried out in methylene chloride, chloroform, or carbon tetrachloride solutions, using polymer concentrations of 1-10g./l. At higher concentrations "gelling" can occur and purification of the product is more difficult. The halogenated polymers were isolated by slowly pouring the solution into a large excess of methanol. The polymer was redissolved and reprecipitated if any retention of a greenish colour was observed. The polymer, washed with methanol was dried under vacuum at 40°C.

When chlorine is allowed to expand from X into Y -

$$\text{Weight Fraction in Y} = \frac{Wy}{W\ \text{Total}}$$

But weight fraction = volume fraction

$$\therefore \frac{Wy}{W\ \text{Total}} = \frac{Vy}{V\ \text{Total}} = \frac{Y}{X + Y}$$

This ratio is known as the delivery fraction and was determined as follows.

Solutions were made up in the reaction vessels, each solution containing 100mls. of $M/_5$ potassium iodide. The solutions were numbered 1-8.

Solution 1 was attached to the chlorination apparatus at the point P, frozen in liquid nitrogen and evacuated. Chlorine was allowed to expand from X to Y with stopcock 2 closed. Stopcock 1 was then closed and stopcock 2 opened. Once the chlorine had been distilled from Y into the reaction vessel, stopcock 4 was closed, the vessel was removed from the line and allowed to thaw. The liberated iodine was estimated by titration against $\frac{M}{1}$ sodium thiosulphate solution. This process was repeated for solutions 2-8 and the results are shown in Table 1.

TABLE 1

Solution Number	Titration Value (mls.)	Ratio of Titration Values	Delivery Fraction D
1	32.40	-	-
2	30.29	0.935	0.065
3	28.45	0.939	0.061
4	26.60	0.936	0.064
5	24.85	0.933	0.067
6	23.05	0.929	0.071
7	21.60	0.936	0.064
8	20.15	0.934	0.066

$$Cl_2 + 2KI \text{ ---------- } 2KCl + I_2$$

$$2Na_2S_2O_3 + I_2 \text{ ---------- } 2NaI + Na_2S_4O_6$$

Using the above equations it follows that 1 ml. of $\frac{M}{1}$ thiosulphate = 35.5 mg. chlorine. The ratio of successive titres obeys the equation.

$$R = \frac{X}{X + Y} = 1 - D$$

where D is the delivery fraction.

CHARACTERISATION OF CHLORINATED POLYBUTADIENE

ELEMENTAL ANALYSIS.

Elemental analysis of carbon, hydrogen, and chlorine, was used to monitor the uptake of chlorine by the polymer. When the reaction was carried out under vacuum using either chloroform or carbon tetrachloride as the solvent, the theoretical percentage for pure addition across the double bond (56.7% Cl_2) was quickly attained, and if the reaction was allowed to continue this figure was soon surpassed. However, when methylene chloride was used as the solvent, the theoretical figure was not surpassed. (see Tables 2 and 3)

TABLE 2

Solvent	Cl-content Wt.-%
CCl_4	56.6
$CHCl_3$	56.4
CH_2Cl_2	55.6

Reaction Time = 1 hour

TABLE 3

Solvent	Cl-content Wt.-%
CCl_4	58.4
$CHCl_3$	57.1
CH_2Cl_2	55.7

Reaction Time = 3 hours

The theoretical figure of 56.7% chlorine was not in fact reached in methylene chloride solution even when the reaction time was extended to fifty hours (see Table 7). This is explained by a small degree of cyclisation of the unsaturated units and is a feature which has also been observed by other workers [10].

INFRA-RED SPECTROSCOPY

Infra Red spectrometry proved to be useful in elucidating the structure of the chlorinated polymers. The spectrum of the chlorinated polymer is shown in Fig. 8 and can be compared to the spectrum of polybutadiene in Fig. 7, and PVC Breon 113 a British Geon polymer, in Fig. 9.

As chlorination proceeds, the bond associated with the C-H stretching mode of an isolated unsaturated group ($3007cm^{-1}$) disappears. Similarly the bands at $1660cm^{-1}$ (C=C stretching) and $735cm^{-1}$ (C-H out of plane bending) also vanish. The band at $1260cm^{-1}$ (also a C-H bending mode) increases sharply while a new band corresponding to C-Cl stretching mode appears at $645cm^{-1}$. The band at $790cm^{-1}$ has been shown by Amagi [11] and co-workers to correspond to $-CH_2-$rocking.

PROTON MAGNETIC RESONANCE SPECTROSCOPY

This technique was used to determine the position of chlorine atoms in the polymer chain. The PMR spectra of polybutadiene and chlorinated polybutadiene are shown in Fig. 10. In the spectrum of pure polybutadiene there are two peaks at 4.5p.p.m. and 7.7p.p.m. in the ratio 1:2 corresponding to the olefinic and methylene hydrogens respectively. Assignment

Fig. 7

I.R. spectrum of polybutadiene

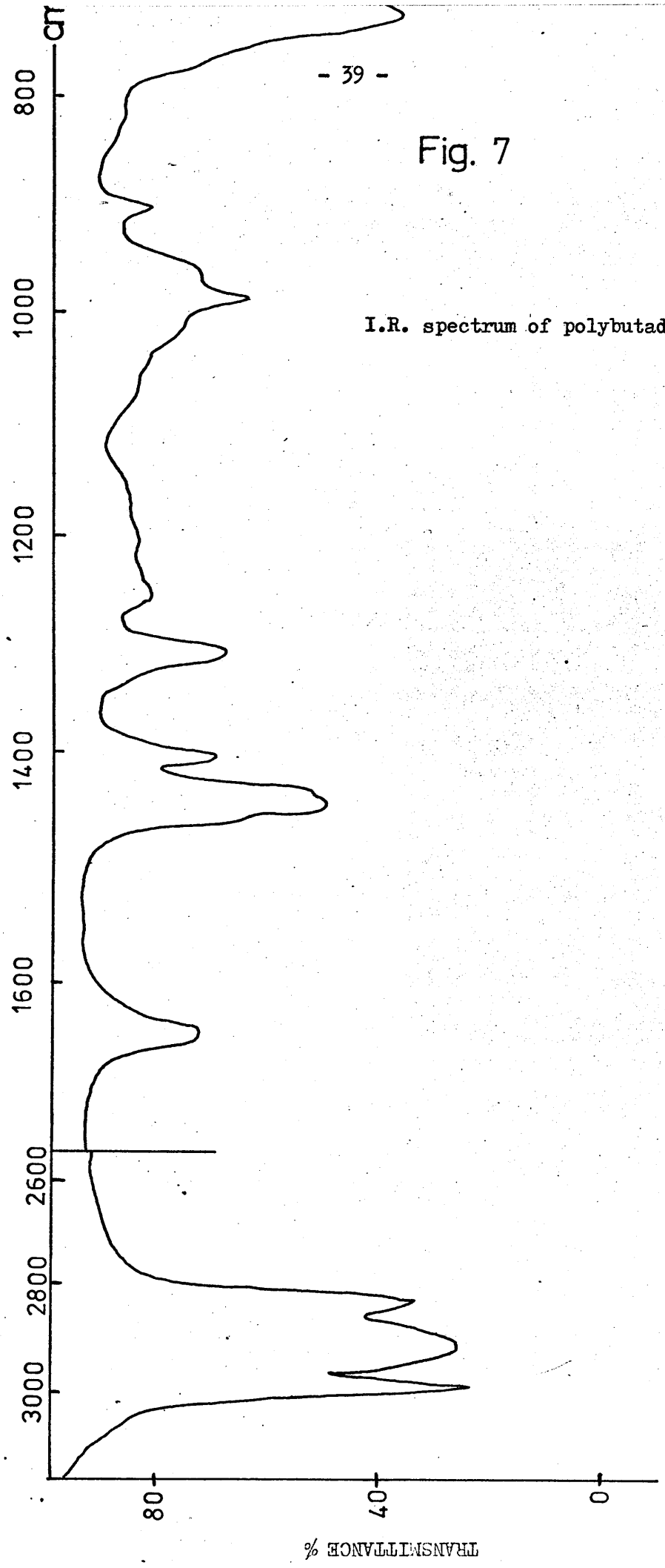
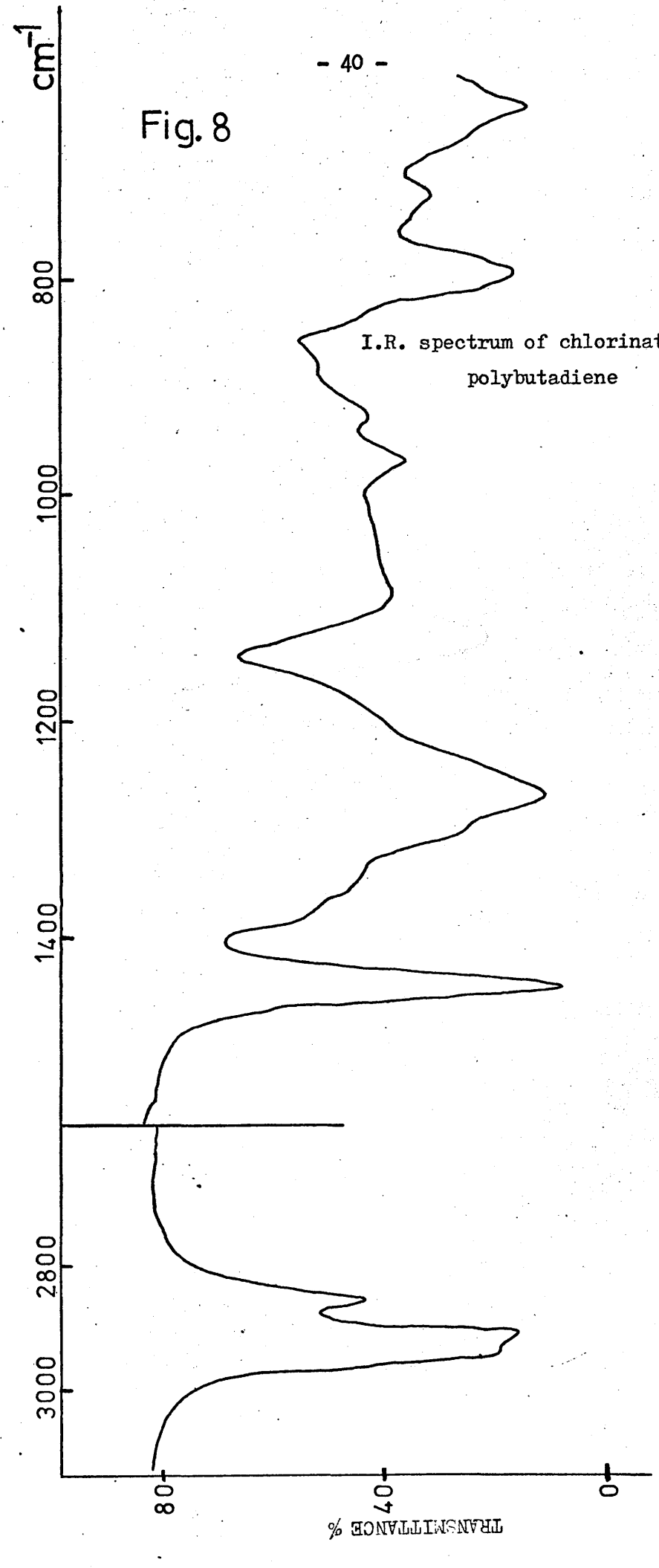


Fig. 8



I.R. spectrum of chlorinated polybutadiene

Fig. 9

I.R. spectrum of PVC Breon 113

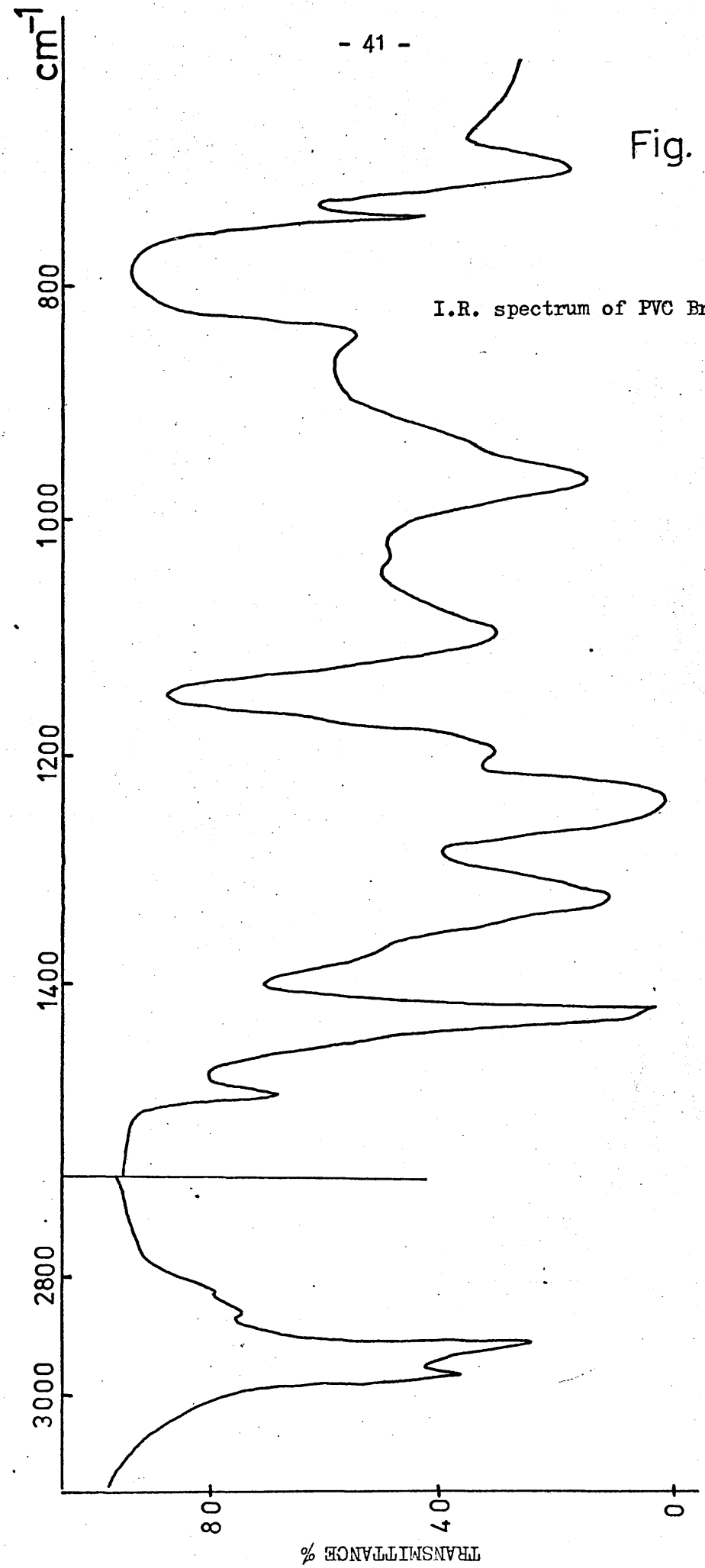
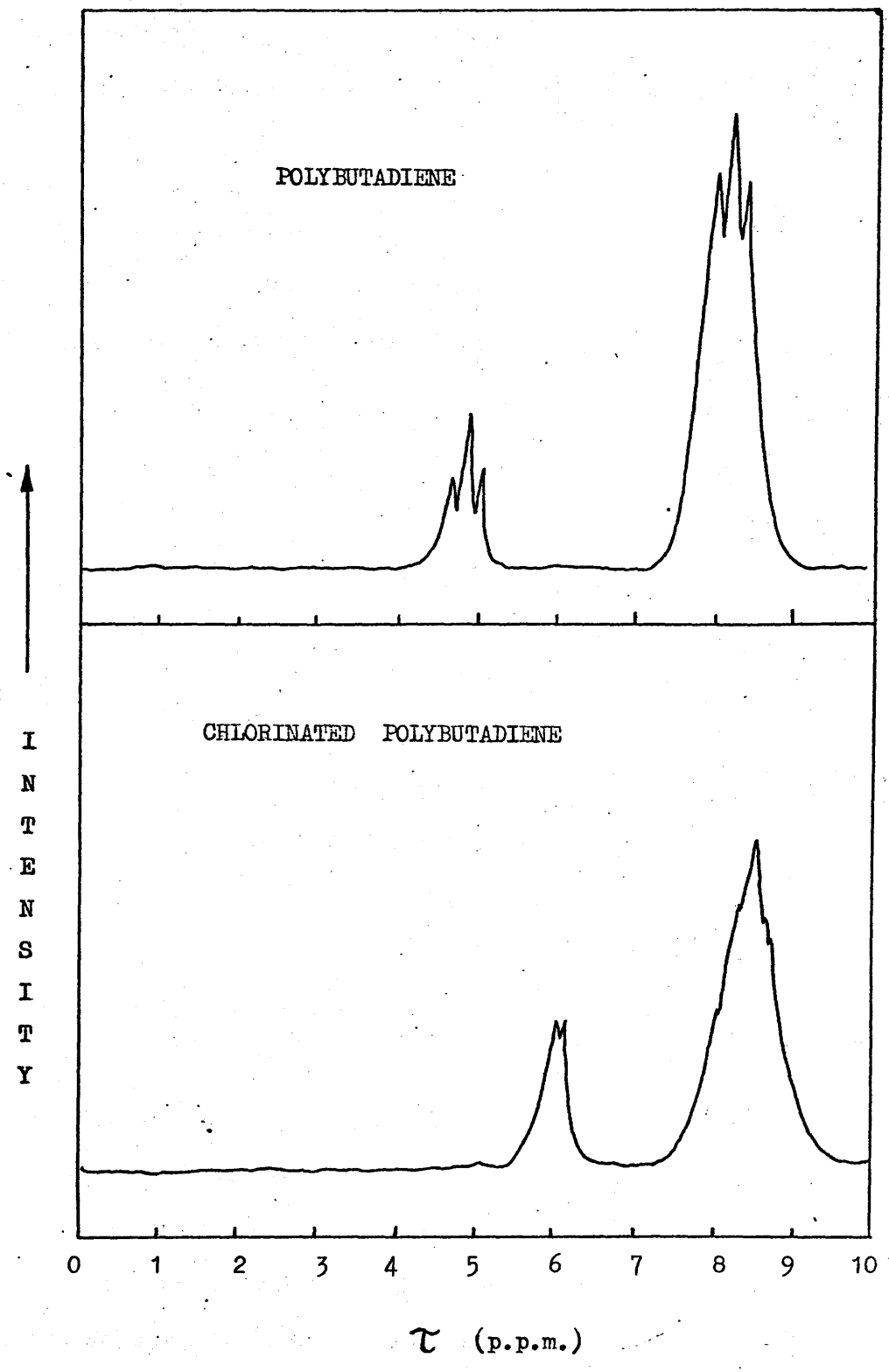


Fig 10 P.M.R. SPECTRA



of structures to new peaks in the chlorinated polymers was made by reference to published τ values[38,39] and previous studies of chlorinated polymers [40,41] and hydrocarbons [42].

The peak at 5.6p.p.m. was attributed to the -CHCl- units. This value is slightly less than that of an isolated -CHCl- group which would appear at 6.1p.p.m.. This is due to the effect of the nearby chlorine which decreases the shielding of the hydrogen atoms and hence causes a shift to lower τ values. The peak at 8.0p.p.m. was attributed to - CH_2 - units. Further information was obtained by examining the area ratio of the peak at 8.0p.p.m. to the peak at 5.6p.p.m. The value for this was 2:1. Hence the only structure which can satisfy the PMR spectrum is the model head-to-head PVC structure.

SIDE REACTIONS

Throughout the series of experiments conducted under vacuum, a small amount of residue always appeared in the polymer solution when it was allowed to thaw. This residue appeared irrespective of the solvent system, was always insoluble and accounted for ~5% by weight of the product. The yield of this residue was greatest for carbon tetrachloride and least for methylene chloride, and increased slightly as polymer concentration in solution was increased. Since the residue was in the form of a rubbery gum when isolated, subsequent characterisation proved difficult. Micro-analysis revealed that the residue generally had the same

chlorine content as the polymer in solution. The residue was therefore thought to be a cross-linked head-to-head PVC structure.

CHLORINATION UNDER NITROGEN AND AIR

A series of experiments similar to those described for vacuum work were carried out under both nitrogen and air atmospheres. Throughout all these chlorinations experiments the results obtained were closely similar to those obtained under vacuum. The only difference was that when the reactions were done either under air or nitrogen, no insoluble material was formed and yields were quantitative. A typical set of results using the three systems is shown in Table 4.

TABLE 4

System Used	Cl-Content Wt.-%
Vacuum	55.6
Nitrogen Atmosphere	55.9
Air Atmosphere	55.7

Time = 1 Hour
Temperature = 20°C
Solvent CH_2Cl_2

As shown in Table 2 previously reactions carried out using methylene chloride as a solvent appear to involve only the addition reaction. Using this system further chlorinations were carried out using time, chlorine concentration, and chlorination temperature as reaction variables.

TEMPERATURE

Pure addition chlorination was observed in the temperature range - 78°C to 20°C as shown in Table 5.

TABLE 5

Chlorination temperature (°C)	Cl-content Wt.-%
-78	55.4
-20	55.8
0	55.6
+20	55.8

Solvent = CH_2Cl_2
Molar Ratio = 1.25:1
Time = 1 hour

Assessment of these results however is difficult since all the reaction mixtures have to warm up from the initial starting temperature of -196°C. Consequently, before the reaction mixture reaches the stated temperature, it has to pass through a wide range of temperature.

CHLORINE CONCENTRATION

Excess of chlorine above the required amount for complete addition chlorination had no appreciable influence on the composition of the chlorinated polybutadiene as shown in Table 6. Chlorinations were carried out where the molar ratio of chlorine:polymer varied from 0.5 : 1 to 10:1.

The results show that no significant change in the composition of the chlorinated polymer was observed over the whole range.

TABLE 6

Molar Ratio	Cl-content Wt.-%
0.5:1	28.3
1.0:1	55.2
1.25:1	55.7
2.5:1	55.8
5.0:1	55.7
7.5:1	55.5
10.0:1	55.7

Solvent = CH_2Cl_2
Temperature = 20°C
Time = 1 hour

It was also observed that with a molar ratio of 1.25:1, complete chlorination was achieved within a very short time. Therefore, this molar ratio was chosen throughout all the series of experiments when other variables were introduced.

TIME

Chlorination reactions were carried out as before, however, longer reaction times were allowed before the reaction product was isolated. The addition chlorination was completed within a short period after the start of the reaction, and prolonged chlorinations did not appreciably alter the chlorine content of the chlorinated polymer as shown in Table 7.

TABLE 7

Chlorination Time (mins.)	Cl-content Wt.-%
15	51.6
30	55.7
60	55.6
300	55.8
600	55.6
3000	55.8

Solvent = CH_2Cl_2
Temperature = 20°C
Molar Ratio = 1.25:1

As can be seen from Table 5, complete addition chlorination was achieved in about 30 minutes. Chlorinations throughout the series therefore were allowed a reaction time of one hour unless otherwise stated.

MOLECULAR WEIGHT STUDIES

All the methods of analysis so far described failed to detect any difference between the products prepared by vacuum techniques and those prepared by reaction under air and nitrogen atmospheres. Since a significant amount of by-product was always formed under vacuum, molecular weight studies were carried out to establish whether cross-linking or degradation processes were affecting the reaction products. Tables 8 and 9 compare the molecular weights of the chlorinated products using the three different methods of preparation. The molecular weights of samples prepared under nitrogen and air atmospheres are close to the calculated values. The experimental values are slightly higher than the calculated ones. This is probably due to a slight loss of low molecular fractions during both chlorination and purification.

TABLE 8

Reaction Conditions	Molecular Weight
Nitrogen Atmosphere	95,000
Air Atmosphere	98,000
Vacuum	152,000

Solvent = CH_2Cl_2

Theoretical molecular weight of the chlorinated polymer = 92,000

TABLE 9

Solvent System	Molecular Weight
CH_2Cl_2	152,000
$CHCl_3$	212,000
CCl_4	244,000

All reactions under vacuum

However, the molecular weight of samples chlorinated under vacuum is markedly different from the calculated values. In all cases, the molecular weight was appreciably higher than the calculated value, although those obtained in methylene chloride solution were lower than either of those in chloroform or carbon tetrachloride. It can be concluded therefore that during the chlorination of polybutadiene under vacuum conditions a competing cross-linking reaction is also occurring. Before deciding whether the cross-linking is radical or Diels Alder in nature, it is worth while to look at some of the experimental data.

(i) Carbon tetrachloride which yields chlorinated samples with the highest molecular weight values is also the solvent which most favours the radical reaction.

(ii) When methylene chloride is used as solvent and even under vacuum conditions, the theoretical chlorine content for addition only is never surpassed.

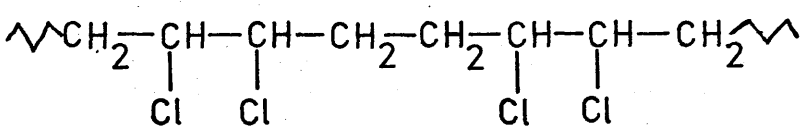
(iii) An insoluble residue is formed only when the reaction is carried out under vacuum .

Since the theoretical chlorine content for addition only is never surpassed, it appears that reactions under vacuum using methylene chloride as a solvent are essentially non-radical in nature. However, under these conditions insoluble material is still formed during the reaction.
Hence the cross-linking process appears to be non-radical in nature, and may be due to a Diels-Alder type process which was mentioned in Chapter 1.

CONCLUSIONS

Chlorination of polybutadiene proceeds by addition across the double bond as long as the reaction is performed in methylene chloride solution. Reactions in both chloroform and carbon tetrachloride yield a product in which some degree of substitution is evident. However, if the reaction is carried out under vacuum, a competing side reaction occurs which causes cross-linking and a subsequent increase in the molecular weight of the chlorinated polymer.

Detailed characterisation by elemental analysis, infra-red spectroscopy and by nuclear magnetic resonance spectroscopy have shown that the chlorinated product corresponds in general to the structure shown over.



The possible presence of cyclic structures has been mentioned previously. However, from the value of the percentage chlorine present in the polymer, it can be seen that there are only 1-2 cyclic ring structures per 100 "vinyl chloride" type units.

Chlorinated polybutadiene therefore prepared under the proper conditions corresponds closely to the model head-to-head poly(vinyl chloride) structure. Hence all subsequent degradation experiments were carried out using samples of polybutadiene which had been chlorinated in methylene chloride under a nitrogen atmosphere and are subsequently referred to as head-to-head PVC.

A short section in Chapter 4 is devoted to the study of the effect mode of preparation of head-to-head PVC has on its degradation behaviour.

CHAPTER 4

THERMAL DEGRADATION OF HEAD-TO-HEAD PVC

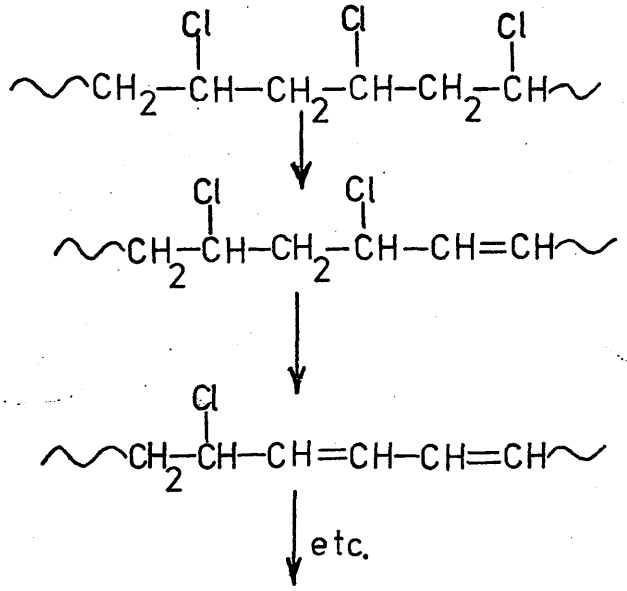
INTRODUCTION

Thermal degradation studies of head-to-head PVC will be discussed fully later in this chapter. It is useful at this stage however, to review the thermal properties of normal head-to-tail PVC, and to discuss the mechanism of thermal degradation in some detail.

THERMAL DEGRADATION OF PVC

A vast amount of research has been done on PVC due to its importance in the commercial field. Particular attention has been paid to its thermal properties, but at the present time there is no general agreement on the nature of the degradation mechanism. Degradation is known to occur by stepwise elimination of hydrogen chloride along the polymer chain, followed by subsequent break-up of the polymer chain at higher temperatures. The elimination reaction produces long sequences of double bonds which confer colouration to the polymer very early in the degradation. The main disadvantage of PVC as a commercial polymer is that processing is difficult since considerable degradation has occurred by the time the melting point of the polymer has been reached. Degradation involves both colouration and the loss of mechanical and electrical properties. It is only when the mechanism of

thermal degradation is fully understood that suitable steps can be taken to ensure the maximum stability and working range of PVC. The general mechanism of breakdown of PVC can be represented as follows :



Once double bonds have been formed, these can activate atoms in allylic positions and hence further enhance the elimination process, with the consequent build-up of long polyene sequences. The thermal degradation of PVC has been comprehensively reviewed by Geddes [43] and Braun [20].

For further discussion of the dehydrochlorination reaction in the degradation of PVC, it is convenient to use the following three headings.

(1) Initiation step

(2) Onset of colour

(3) Mechanism of dehydrochlorination

(1) INITIATION

Investigations with model compounds have shown that PVC is in fact less stable than predicted. Model compounds required an activation energy of about 50 Kcals./mole with dehydrochlorination occurring at 350° - 400°C. [44] Since PVC requires an activation energy of 30 Kcals./mole with dehydrochlorination occurring at 225° - 350°C., it follows that PVC must contain irregularities or impurities in structure which act as sites of initiation. Possible irregularities can be classified as follows:-

(a) Head-to-head units.

(b) Peroxide structures.

(c) Chain branches with tertiary chlorine atoms.

(d) Random unsaturation.

(e) Chain-end groups.

Although head-to-head units have not yet been identified in PVC, Wilson and co-workers [5] have shown that poly(vinyl fluoride) contains as many as 1 in 6 head-to-head units. Some work has been done using chlorinated polybutadiene as a model compound [10]. Vicinal chlorine atoms have been shown to be more thermally labile than their 1,3 counterparts. Hydrogen chloride loss begins sooner than in pure PVC but the rate of elimination is slower. This reaction will be discussed in much greater detail in the later stages of this chapter. Peroxide or hydroperoxide structures are thought to be formed by the oxidation of PVC. In the subsequent decomposition reaction carbonyl compounds are formed and these absorptions

have been observed in the infra red spectra [45]. It has also been shown that the rate of dehydrochlorination increases with increased oxygen content [46]. It is thought therefore that these peroxide structures may break down to form radicals which may in turn initiate hydrogen chloride elimination by a radical mechanism.

Chain-branches have been considered to be sites for initiation if tertiary chlorine atoms are also present. Although a significant degree of branching has been observed in PVC [47], more recent work has shown that the existence of tertiary chlorine atoms at these sites is very unlikely [48,49].

The study of low molecular weight model compounds has shown that random unsaturation with allylic chlorine atoms produces thermal lability. More recently, using PVC samples, Braun and Quarg observed a direct correlation between random unsaturation and rate of dehydrochlorination [50]. It was shown that in the early stages of degradation, one polyene sequence was formed from each isolated double bond. In addition the average length of the polyene sequence could be calculated and the results obtained were in good agreement with observed spectroscopic data.

The importance of unsaturated end-groups and their effect on PVC degradation has aroused much controversy. Their presence has been demonstrated conclusively by Bengough [51]. However, conflicting evidence has been presented by various workers as to their relative importance as initiation sites. Baum

and Wartmann [52] have concluded that initiation occurs mainly at chain-ends, whereas Braun and Quarg [50] have demonstrated the importance of random double bonds as initiation sites.

(2) ONSET OF COLOUR

Colouration is the first apparent sign of degradation in PVC and it appears before any of the other effects of degradation are obvious. Colouration deepens as degradation proceeds and is consistent with the formation of long polyene sequences; however, as yet no quantitative relationship between colour and hydrogen chloride evolution has been formulated. Using the Beer-Lambert law, Thallmaier and Braun[53] calculated that polyene sequences comprising five double bonds were most common in the early stages of degradation, while the longest sequences contained thirty double bonds in conjugation. Surprisingly, sequence length did not increase with the extent of degradation. This can be explained by the onset of cyclisation and cross-linking reactions. The authors concluded that dehydrochlorination begins simultaneously at many sites.

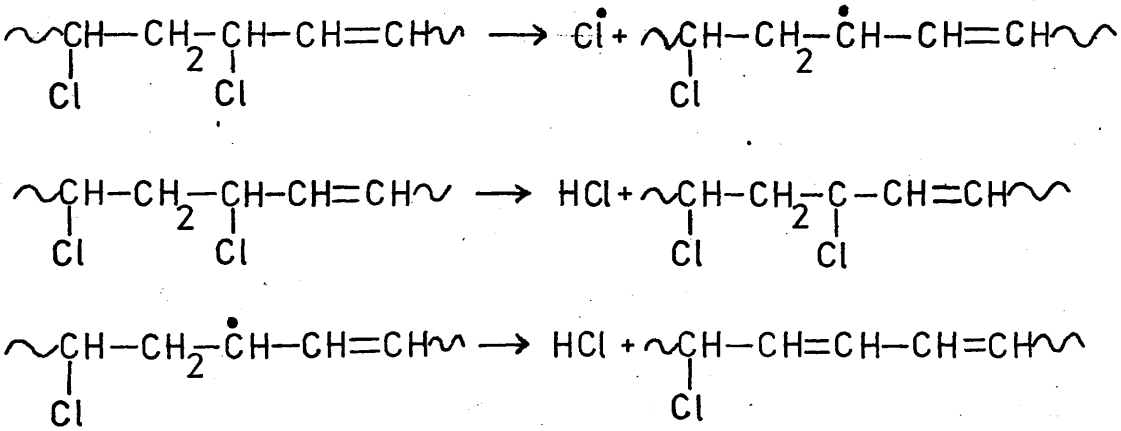
(3) MECHANISM OF DEHYDROCHLORINATION

The mechanism of dehydrochlorination of PVC is still unresolved. Radical, ionic and unimolecular mechanisms have all been proposed by various workers but no conclusive evidence has been

presented for any one of these mechanisms. It is possible that more than one mechanism may be in operation, and this may in fact account for the often conflicting experimental observations.

(i) Radical Mechanism

Stromberg[54] and Bamford[55] have both proposed a mechanism for a radical degradation.



Bamford, in a study of the degradation of PVC in tritium labelled toluene, found incorporation of the tritium into the polymer chain and a linear relation between extent of incorporation of tritium and the rate of dehydrochlorination. However, Bengough and Sharpe[56] have shown that degradation of PVC in an inert solvent was unaffected by the presence of free radical inhibitors. The evidence most relevant to this project has been presented by McNeill and Neill[37], who have shown that PMMA degraded in the presence of PVC is initially less stable with monomer production occurring at a temperature corresponding to dehydrochlorination of PVC.

To explain this observation, they proposed that chlorine radicals from the degrading PVC diffuse into the PMMA phase, and by abstracting a hydrogen atom these radicals can initiate early depropagation of PMMA.

(ii) Ionic Mechanism

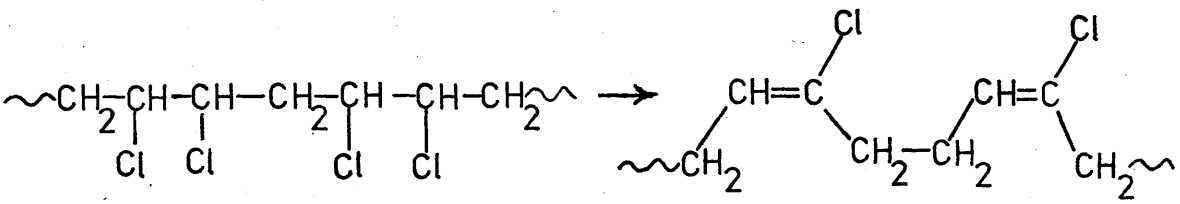
The dehydrochlorination of PVC at 80°C by bases such as lithium chloride in dimethylformamide follows an ionic mechanism[57]. In addition, proton donors such as sulphuric acid, alcohols and phenols have been shown to accelerate the dehydrochlorination[58], while Marks and co-workers[59] have discovered a relationship between the di-electric constant of the solvent and the rate of degradation in solution. Thus it appears that PVC exhibits an ionic type degradation mechanism when subjected to "ionic" influences. However, this does not necessarily prove that in the absence of these influences PVC will still degrade by an ionic type mechanism.

(iii) Unimolecular Mechanism

Braun and Bender[60] have shown when PVC is degraded in an inert solvent and under an inert atmosphere, dehydrochlorination follows a first order rate law. A cyclic intermediate state was postulated which allows the reaction to proceed by stepwise elimination with allylic activation of the chlorine atoms.

PREVIOUS WORK ON THE THERMAL DEGRADATION OF HEAD-TO-HEAD PVC

Very little work has been reported on the degradation of head-to-head PVC. The most significant is that of Murayama and Amagi[10] who showed that the rate of loss of hydrogen chloride from head-to-head PVC was slower than from head-to-tail PVC, although degradation does commence at a lower temperature. The authors produced two main conclusions. Firstly that dehydrochlorination commenced earlier because of the presence of vicinal chlorine atoms. Secondly, the rate of dehydrochlorination is slower due to the formation of the structure shown below.



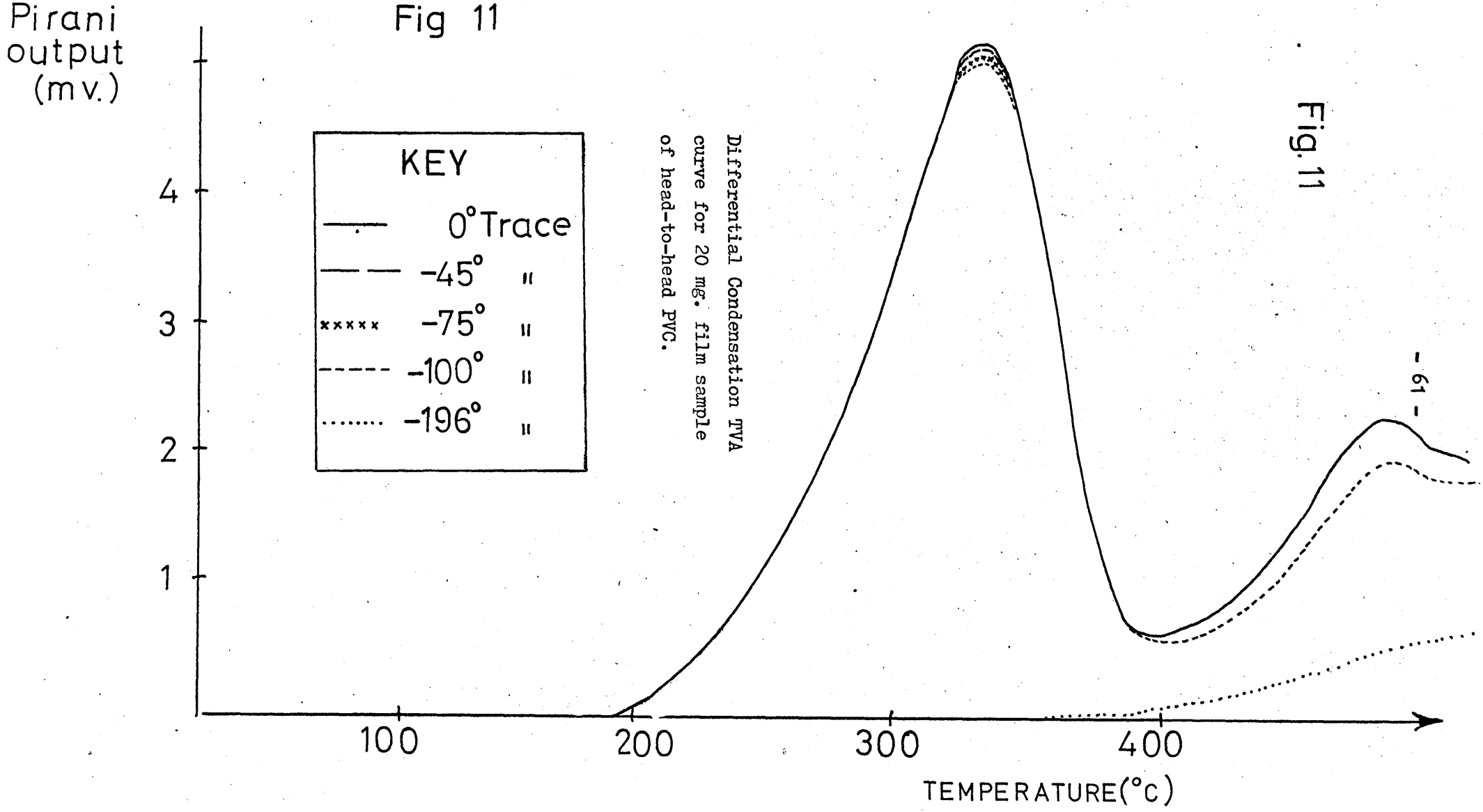
However, Ito and co-workers[12], by means of pyrolysis-gas chromatography have confirmed that chlorinated polybutadienes do have the true head-to-head PVC structure. However, the mechanism of degradation which these authors have proposed involves the formation of conjugated polyene sequences.

THE THERMAL DEGRADATION OF HEAD-TO-HEAD PVC

The experimental methods used to study the thermal degradation of head-to-head PVC were mainly Differential Condensation Thermal Volatilisation Analysis and Thermogravimetric Analysis, both of which have been described previously in Chapter 2. Degradation experiments were conducted on both types of PVC polymer so that valid comparisons could be made of their degradation behaviour. The TVA curve, at a heating rate of 10°/minute for a film sample of head-to-head PVC is shown in Fig. 11. It comprises two peaks, the major one having a $T_{max.}$ of 325°C. and the secondary a $T_{max.}$ of 456°C ($T_{max.}$ value corresponds to the temperature at which the peak maximum occurs).

Degradation commences at the relatively low temperature of 190°C with smooth evolution of material which is volatile at -100°C but fully condensed at -196°C. The major peak is asymmetric in shape with the larger peak area being on the low temperature side of the $T_{max.}$ The secondary peak contains material which is volatile at -196°C. Since the shape of the major peak is broader than that normally observed for a single stage reaction, it is possible that more than one type of reaction process is involved below 400°C. Hence, the overall shape of the TVA curve of head-to-head PVC is indicative of a reaction involving at least two stages, and can be compared with the TVA curve obtained for PVC Breon 113 in Fig. 12. There are several significant differences between the two curves. The main peak in the TVA curve of PVC Breon 113,

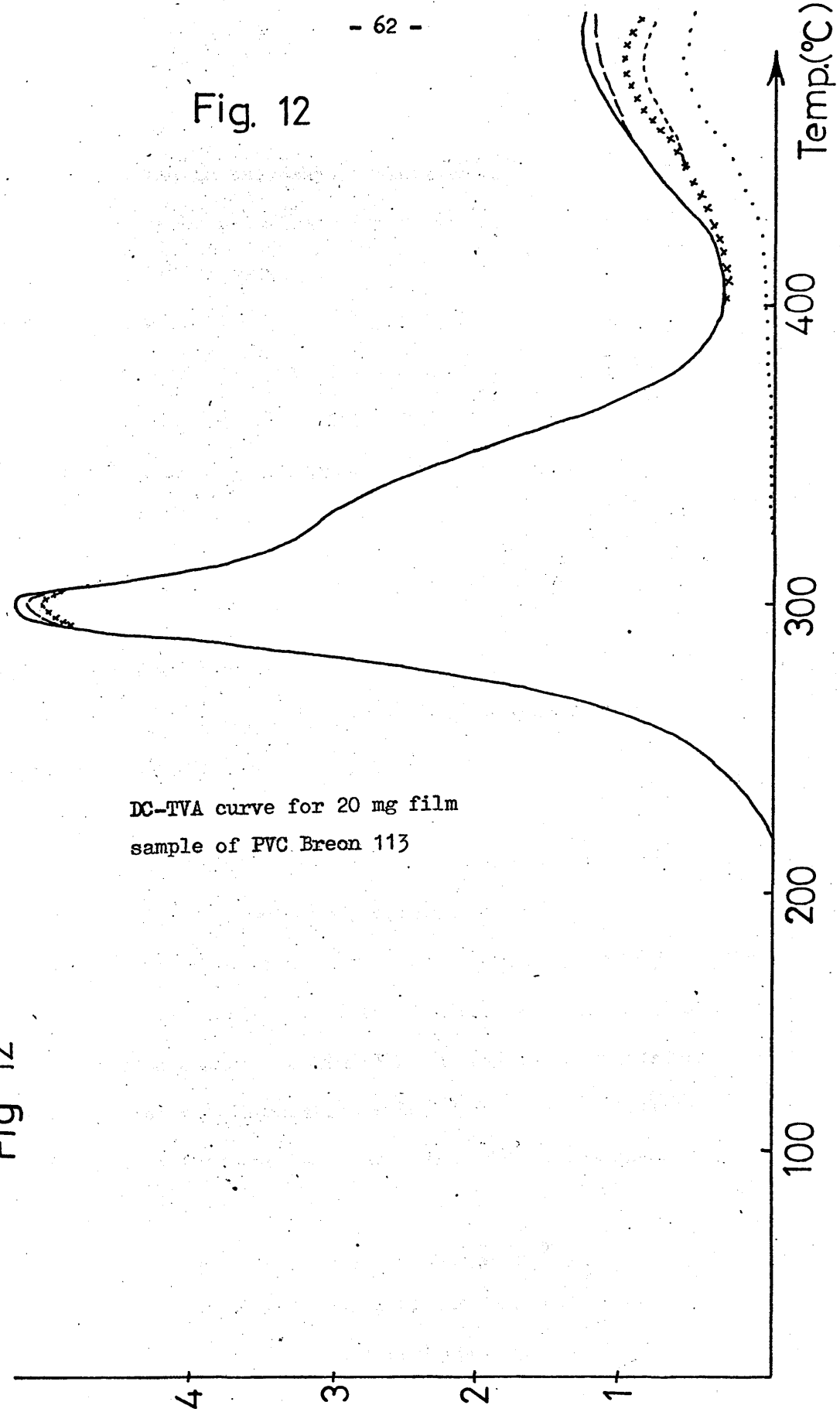
Fig 11



Differential Condensation TVA curve for 20 mg. film sample of head-to-head PVC.

Fig. 11

Fig. 12



DC-TVA curve for 20 mg film sample of PVC Breon 113

Fig 12

corresponding to the dehydrochlorination, shows a distinct two stage reaction. Evolution of material starts later in the Breon 113 trace while the T_{max} is observed at the lower temperature of 310°C. Finally, there is far less non-condensable material evolved in the 400° - 500° range in the degradation of Breon 113. Full details of the identification of the products of degradation will be given later in this chapter.

SAMPLE FORM EFFECT

This was investigated by degrading polymer samples in the form of powders and films. The TVA curves obtained for head-to-head PVC are shown in Fig. 13. The evolution of volatile products commences approximately 20° earlier from the powder sample. In addition, the curve is broader in appearance, although there is no noticeable change in the T_{max} value. Further studies were carried out using a special degradation tube to investigate the effect of film thickness on the degradation of head-to-head PVC. By varying the internal diameter of the degradation tube, films of different thickness could be cast on the base. Approximate film thicknesses are shown in Fig. 14.

As film thickness increases, no change in T_{max} is observed; however, a general broadening of the peak occurs through the series with evolution of material non-condensable at -100°C starting at lower temperatures as the thickness of the film increases. These results can be compared with those obtained

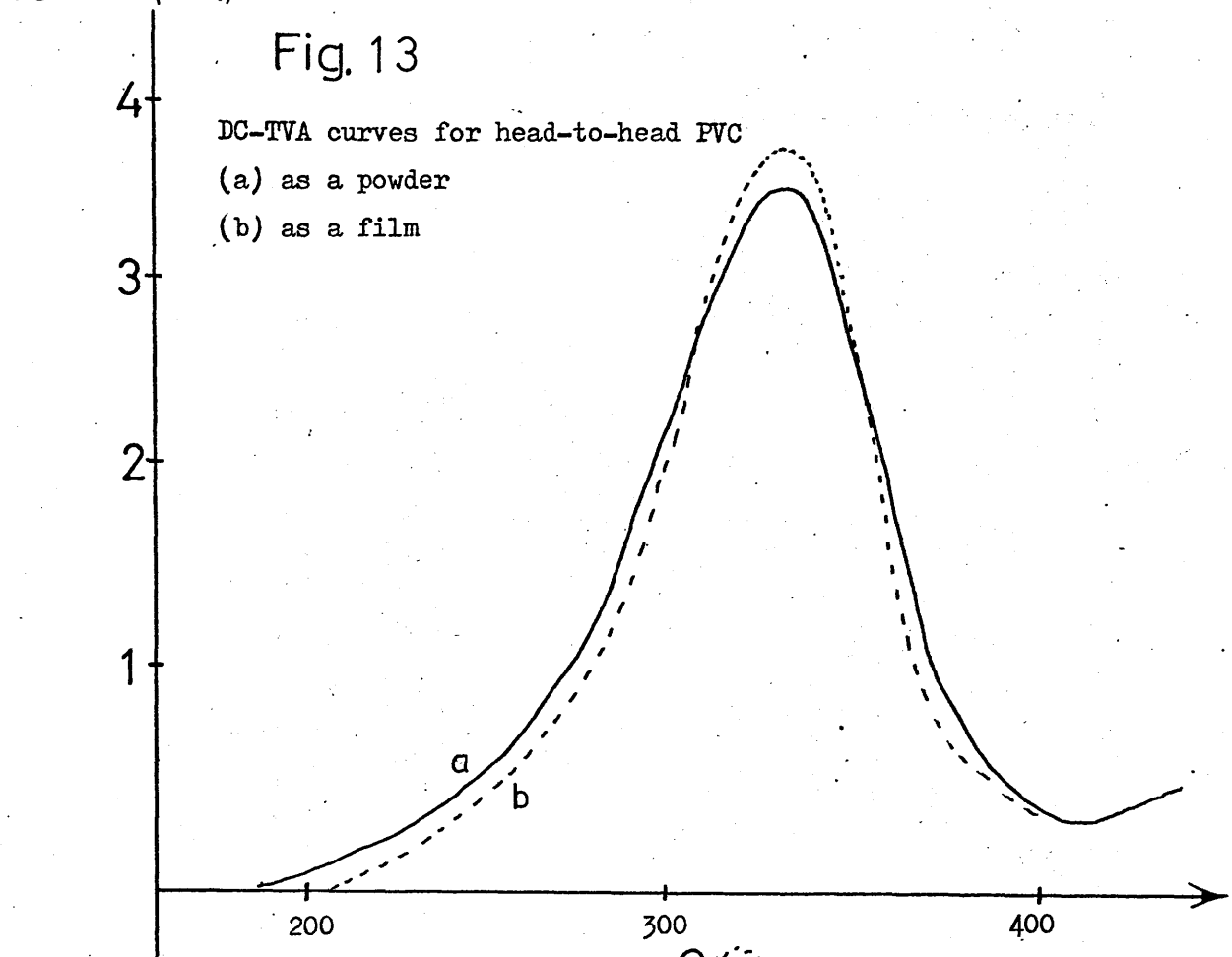


Fig. 13

DC-TVA curves for head-to-head PVC
(a) as a powder
(b) as a film

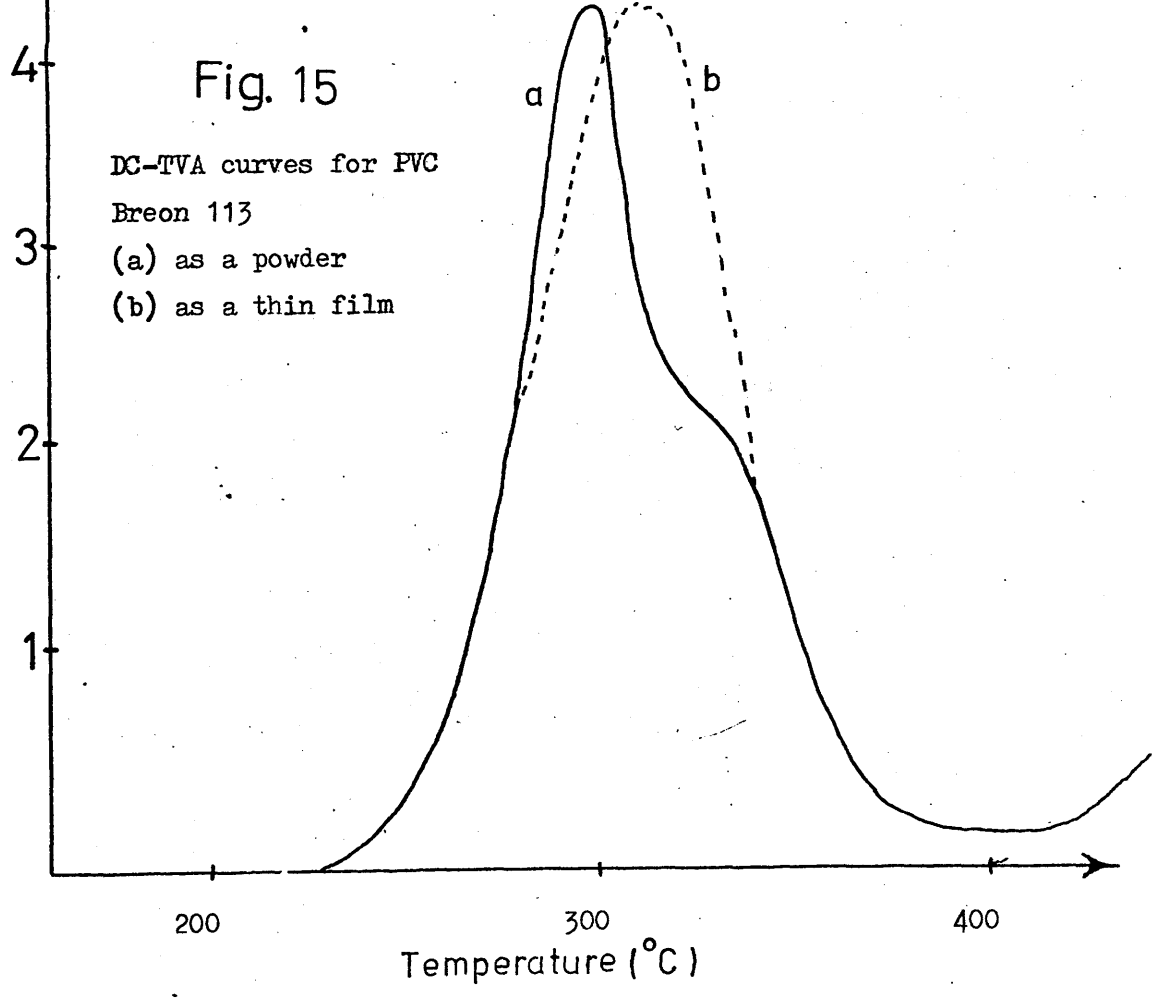


Fig. 15

DC-TVA curves for PVC
Breon 113
(a) as a powder
(b) as a thin film

Fig 14

Film thicknesses obtained using a degradation tube of variable diameter.

Diameter of degradation tube (cms)	Area of base of degradation tube (sq. cms)	Thickness of polymer film(2 mg) (μ)
0•5	0•20	62•5
0•9	0•64	19•5
1•2	1•13	11•0
1•8	2•54	4•9
3•6	9•90	1•3

for powder and film samples of PVC Breon 113. In this case, as the sample form is changed, not only the shape of the curve is changed but also the position of the T_{max}. However the temperature of commencement of degradation is unaltered by sample form. The TVA curves for powder and film samples of Breon 113 are shown in Fig. 15.

The complexity of the breakdown of Breon 113 has been attributed to the effect of catalysis by hydrogen chloride, diffusing through the sample[61]. Diffusion through a powder or thick film is relatively slow, hence hydrogen chloride is trapped within the sample and accelerates the rate of degradation. A similar type of effect seems to be occurring in head-to-head PVC although the fact that T_{max} value does not change can be attributed to its slower rate of dehydrochlorination.

EFFECT OF METHOD OF CHLORINATION ON THE DEGRADATION PROPERTIES OF THE POLYMER

The effect of mode of preparation of the head-to-head PVC was investigated by degrading samples using the TVA apparatus. TVA curves were obtained at 10°/min. for samples prepared under nitrogen and vacuum conditions. The curves obtained, however, were identical in all respects. Hence this provides further evidence that the basic structure of the polymer is unaltered by the mode of preparation as long as methylene chloride is used as the solvent. In addition, samples of higher molecular weight show no appreciable differences in their TVA behaviour.

THERMOGRAVIMETRIC ANALYSIS

Due to the small size of the sample pan and the relatively low density of film samples, thermogravimetric curves were obtained using only crushed powders. The TG curve for head-to-head PVC at a heating rate of 10°/min. is shown in Fig. 16. A two-stage weight loss is observed corresponding to the two peak pattern in the TVA curve. The polymer starts to degrade at 175°C and weight loss is fairly smooth until the polymer has lost approximately 58% by weight at 385°C.

The curve then flattens slightly up to 450°C when the weight loss increases quite sharply leaving a residue of 22% by weight of the polymer at 500°C.

The TG curve obtained from the degradation of PVC Breon 113 is shown in Fig. 17. Again, a two-stage weight loss is apparent, however degradation commences at a much higher temperature (230°C). Weight loss is fairly rapid so that the sample has lost approximately 60% by weight at 350°C. A virtually smooth plateau region is observed between 350°C and 425°C, while above this temperature the weight loss increases sharply to leave a 10% by weight residue at 500°C.

Comparison of the two curves confirms the result of the TVA experiments showing earlier degradation and slower elimination of hydrogen chloride by the head-to-head sample.

One surprising feature of the TG curve is the amount of residue left from the head-to-head sample. From the TVA curves, it appears that head-to-head PVC gives off more

Fig 16

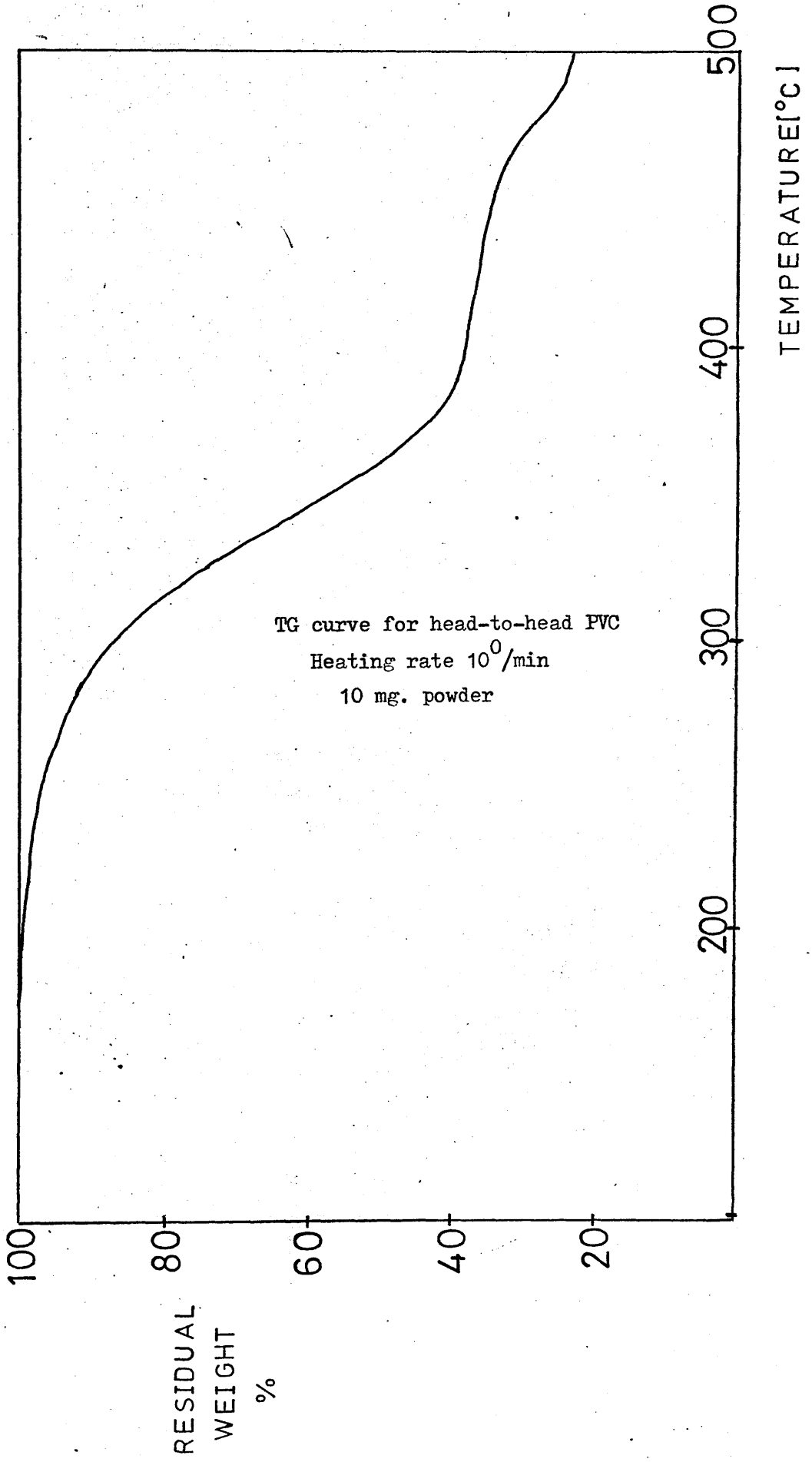
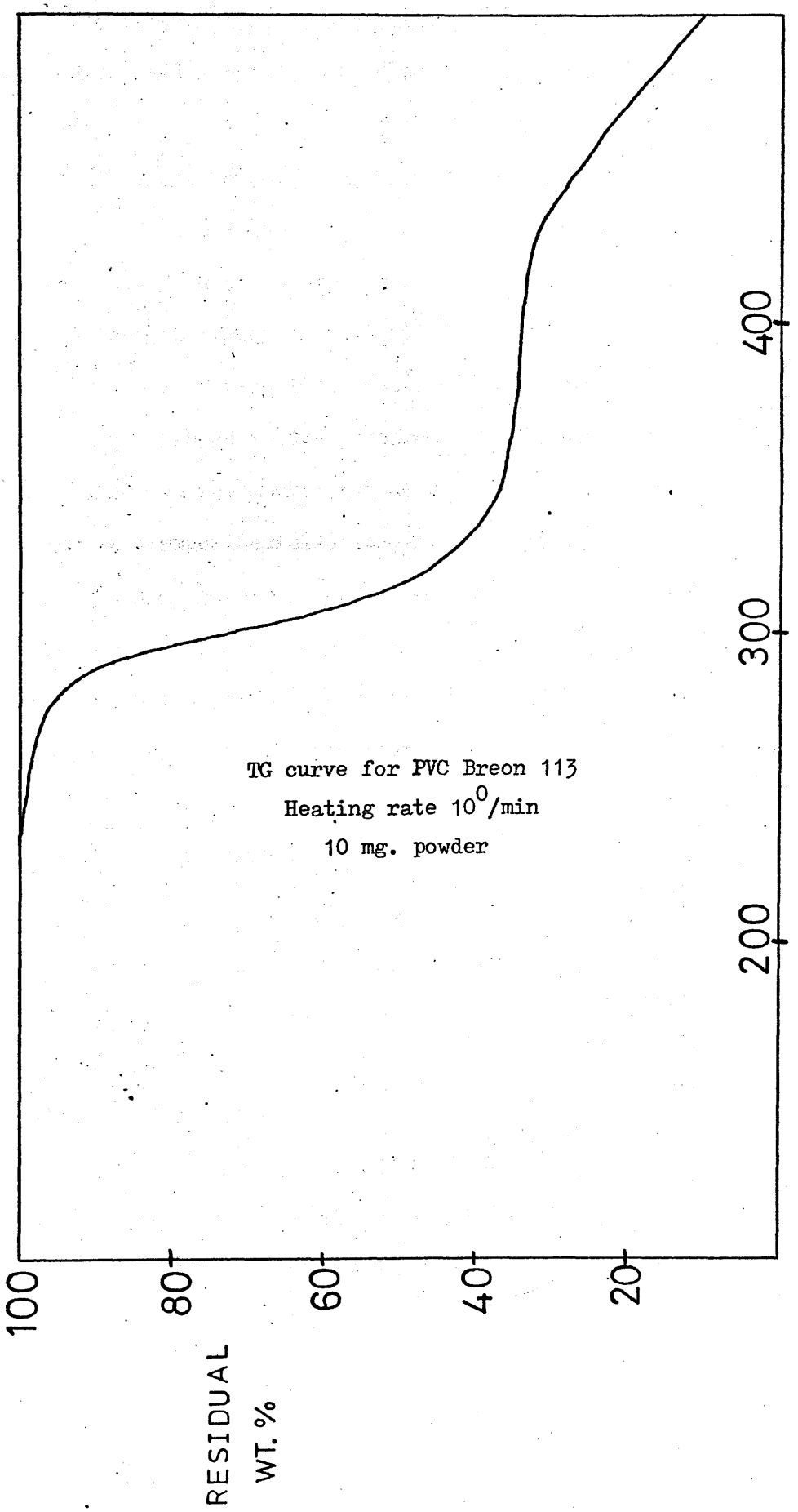

TG curve for head-to-head PVC
Heating rate 10°/min
10 mg. powder
RESIDUAL WEIGHT %
100
80
60
40
20
TEMPERATURE[°C]
500
400
300
200

Fig. 17


TG curve for PVC Breon 113
Heating rate 10°/min
10 mg. powder
RESIDUAL WT. %
100
80
60
40
20
200
300
400
TEMPERATURE [°C]

material in the later stages of degradation, but the residue from the head-to-head sample is significantly greater than from PVC Breon 113.

Since it was difficult to correlate results obtained by TVA under vacuum and TG under dynamic nitrogen atmosphere, a new technique was tried which incorporated both methods. A Cahn model RG thermobalance was introduced into the TVA system so that simultaneous TVA and TG curves (under vacuum) could be obtained. Any changes in the pattern of behaviour under nitrogen and under vacuum could then be detected. The curve obtained from this experimental arrangement is shown in Fig . 18 . However, the results obtained are virtually identical to those obtained using a conventional TG arrangement. The only significant difference occurs in the case of the head-to-head polymer where the secondary reaction appears to be levelling off under vacuum, while under nitrogen this reaction is still in progress.

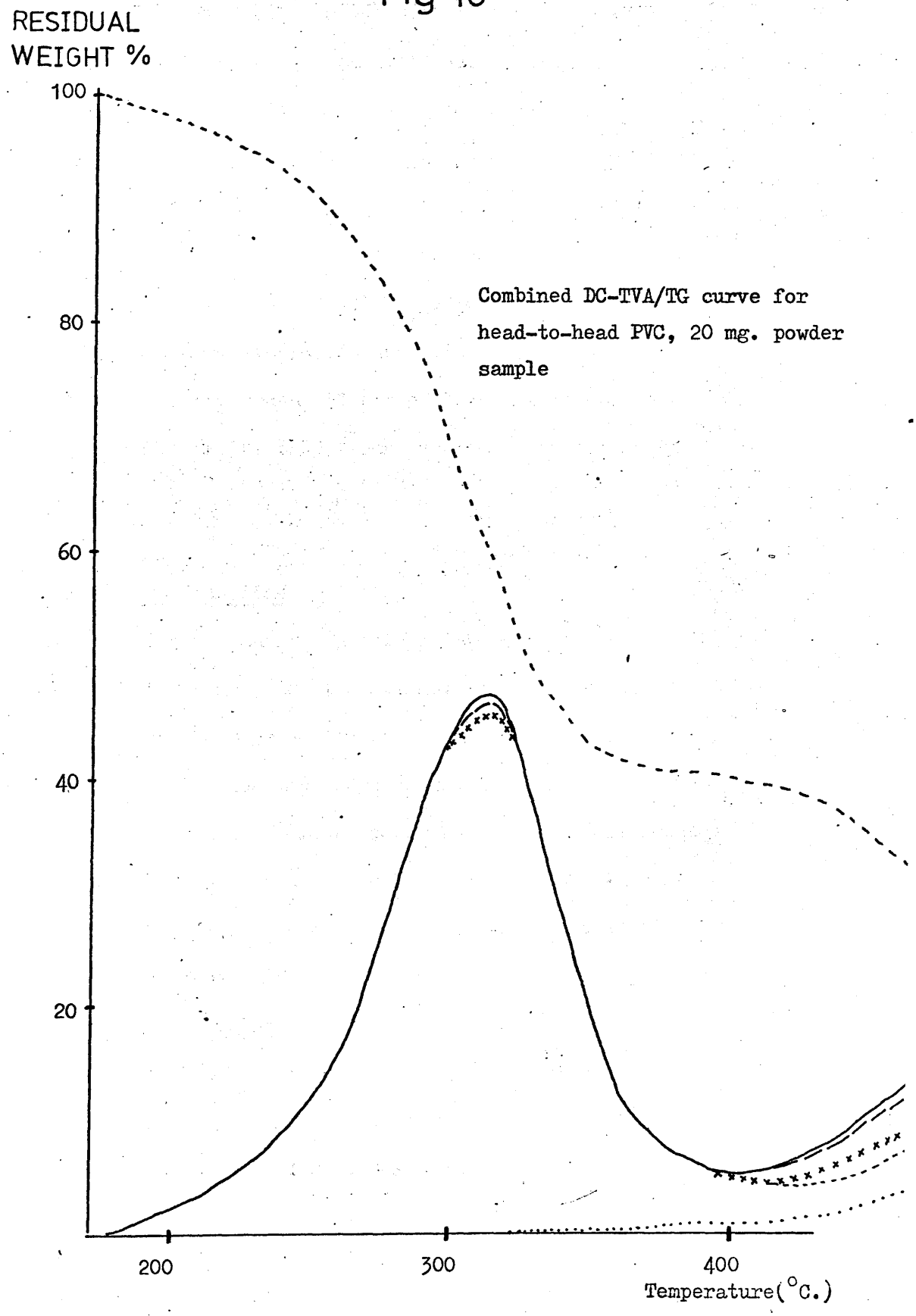
PRODUCTS OF DEGRADATION OF HEAD-TO-HEAD PVC

(1) Volatile Products

(a) Condensables:

Degradation in the TVA apparatus was stopped after the main peak at 385^{o}C and the products collected in the liquid nitrogen and other traps were distilled into a gas cell for infra red analysis. From the spectrum obtained it was

Fig 18



Combined DC-TVA/TG curve for head-to-head PVC, 20 mg. powder sample

concluded that the only product present was hydrogen chloride, which is easily recognised by its characteristic absorption at 3000cm $^{-1}$. A second sample of head-to-head PVC was degraded, however this time products were collected in the temperature range 385^{o}C to 500^{o}C.

Infra red analysis revealed the presence of small amounts of ethylene (950cm $^{-1}$), propylene (920cm $^{-1}$), benzene and hydrogen chloride. Infra red analysis of the products of degradation of PVC Breon 113 showed large quantities of hydrogen chloride but only trace amounts of ethylene and benzene.

(b) Non-condensables:

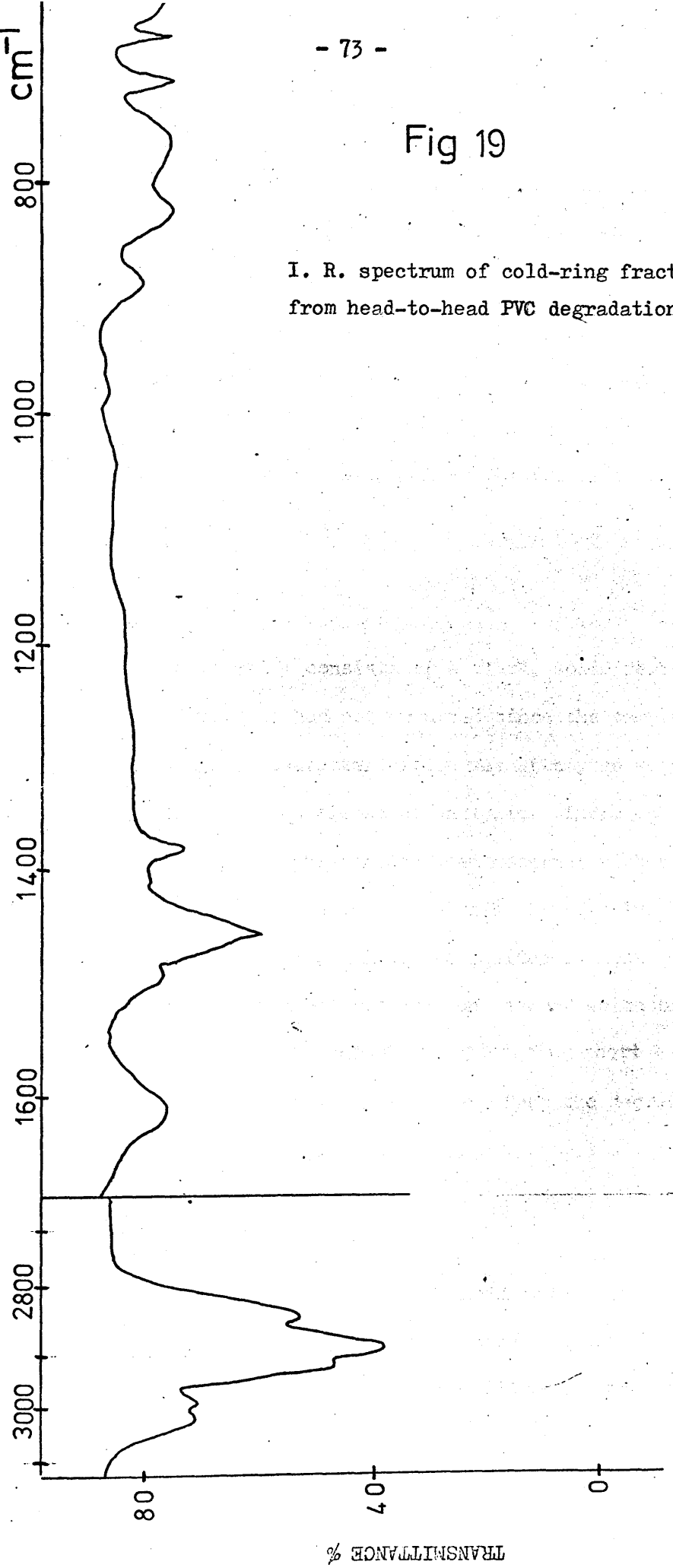
Degradation was carried out in a "closed" evacuated system instead of the conventional continuously pumped system. Products from the degradation were collected in a gas cell and an infra red spectrum was taken with a liquid nitrogen trap in position round the cold-finger. In this way, all condensable material was removed from the cell. Analysis showed only the presence of methane, characterised by absorptions at 1320cm $^{-1}$), and fine structure centred on 3020cm $^{-1}$).

(2) Cold Ring Fraction

The cold ring fraction appeared as a waxy, brown solid on the cooled upper part of the degradation tube. This substance was removed and examined by infra red spectroscopy. The spectrum in Fig. 19 showed strong absorptions at 3020cm^{-1}, 3060cm^{-1} and 1605cm^{-1}, indicating unsaturation. In a second

Fig 19

I. R. spectrum of cold-ring fraction from head-to-head PVC degradation



experiment, heating was stopped as soon as hydrogen chloride evolution had ceased and the tube was allowed to cool. Under these circumstances no cold ring fraction was observed. Hence the cold ring fraction corresponds to the break-up of the polymer backbone and consists of conjugated, low molecular weight fragments. The cold ring fraction obtained for PVC Breon 113 was identical to that obtained for the head-to-head polymer.

(3) Non-Volatiles

The non-volatile material consists of a black, solid residue. It appeared that melting had not occurred since the sample form had not changed. Characterisation was attempted using infra red spectroscopy and elemental analysis. Infra red analysis showed only a highly unsaturated material with strong absorption at 1660cm^{-1}. Elemental analysis showed only carbon and hydrogen present. Hence the residue is most probably a highly unsaturated hydrocarbon network which breaks down in the later stages of degradation producing short chain and aromatic fragments. The residue from the degradation of PVC Breon 113 is essentially similar.

ULTRA VIOLET SPECTROSCOPY

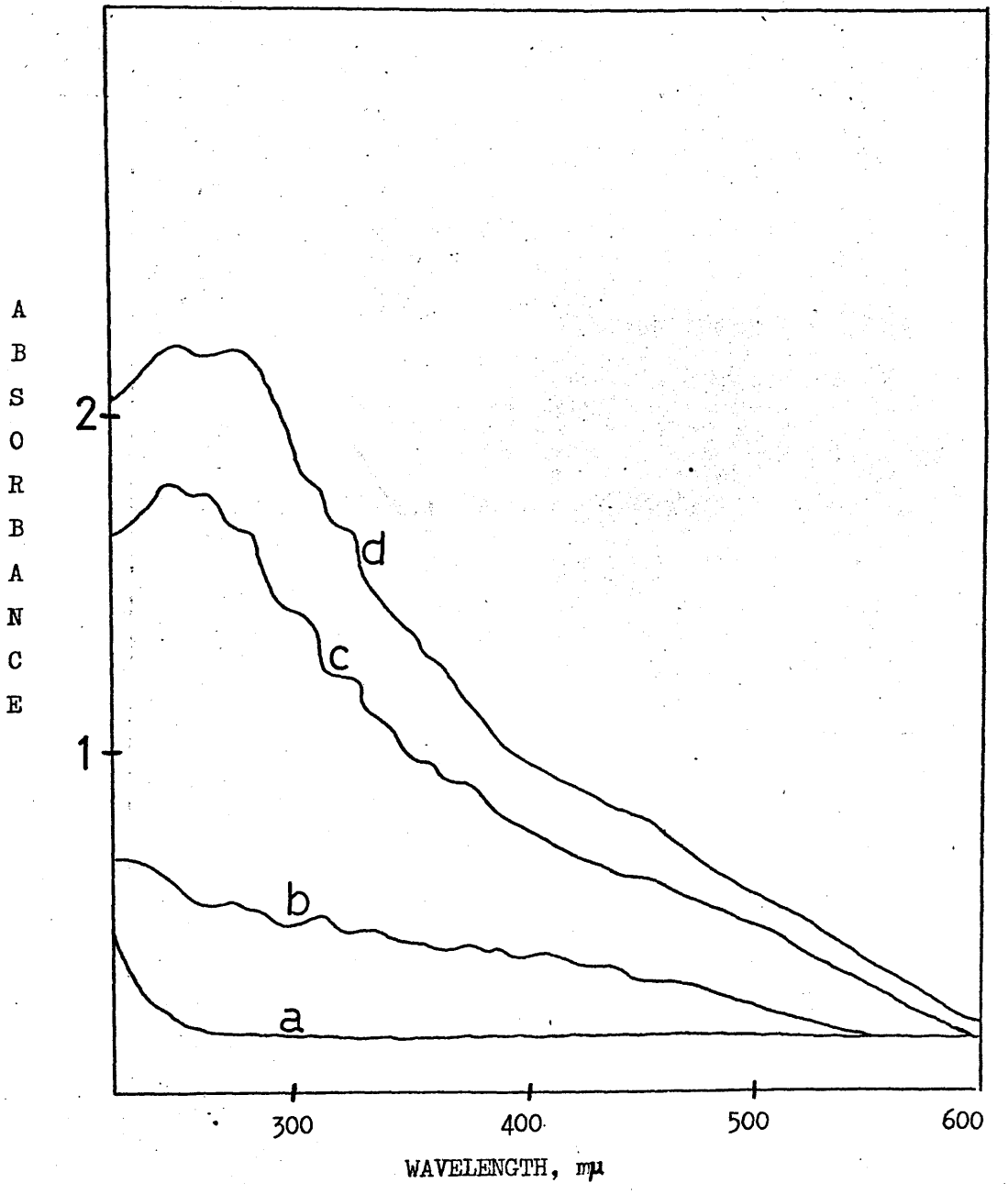
UV spectroscopy was used to characterise the molecular structure of head-to-head PVC in the early stages of degradation. Since the polymer became insoluble as soon as degradation commenced, it was not feasible to record UV spectra in solution cells. A special silica TVA tube was used which

has been described previously in Chapter 2. Cyclohexanone was used to make solutions from which films were cast on to the base of the special degradation tube by vacuum evaporation. Temperature programmed heating was commenced and at certain temperatures degradation was stopped and the sample tube was removed from the oven and placed directly in the UV spectrometer. The spectra of a degraded head-to-head PVC film sample are shown in Fig. 20. A multi-peak pattern is observed even in the early stages of degradation with peak maxima at 230, 275, 285, 320, 350, 390, 415, 440mμ. respectively. In addition, absorption ranges from 225mμ. as far as 575mμ. almost as soon as degradation commences. However, as degradation proceeds there is no obvious movement to higher wavelength values. Instead the absorption intensifies and gradually moves off scale. Further experiments were carried out at 170°, 175° and 180° using isothermal heating. Similar sets of spectra were obtained in every case. Before the spectra of head-to-head PVC are discussed, it is worthwhile to consider the UV spectra of PVC Breon 113, the head-to-tail polymer.

A similar experimental arrangement was used to obtain a set of UV spectra for degraded PVC Breon 113 samples. These are shown in Fig. 21 and are in general agreement with results obtained by previous workers.[53,62,63]. A multi-peak pattern is observed with maxima occurring at 235, 267, 279, 290, 312, 327, 342, 366, 390, 414, 440, 464 and 480mμ respectively. Absorption

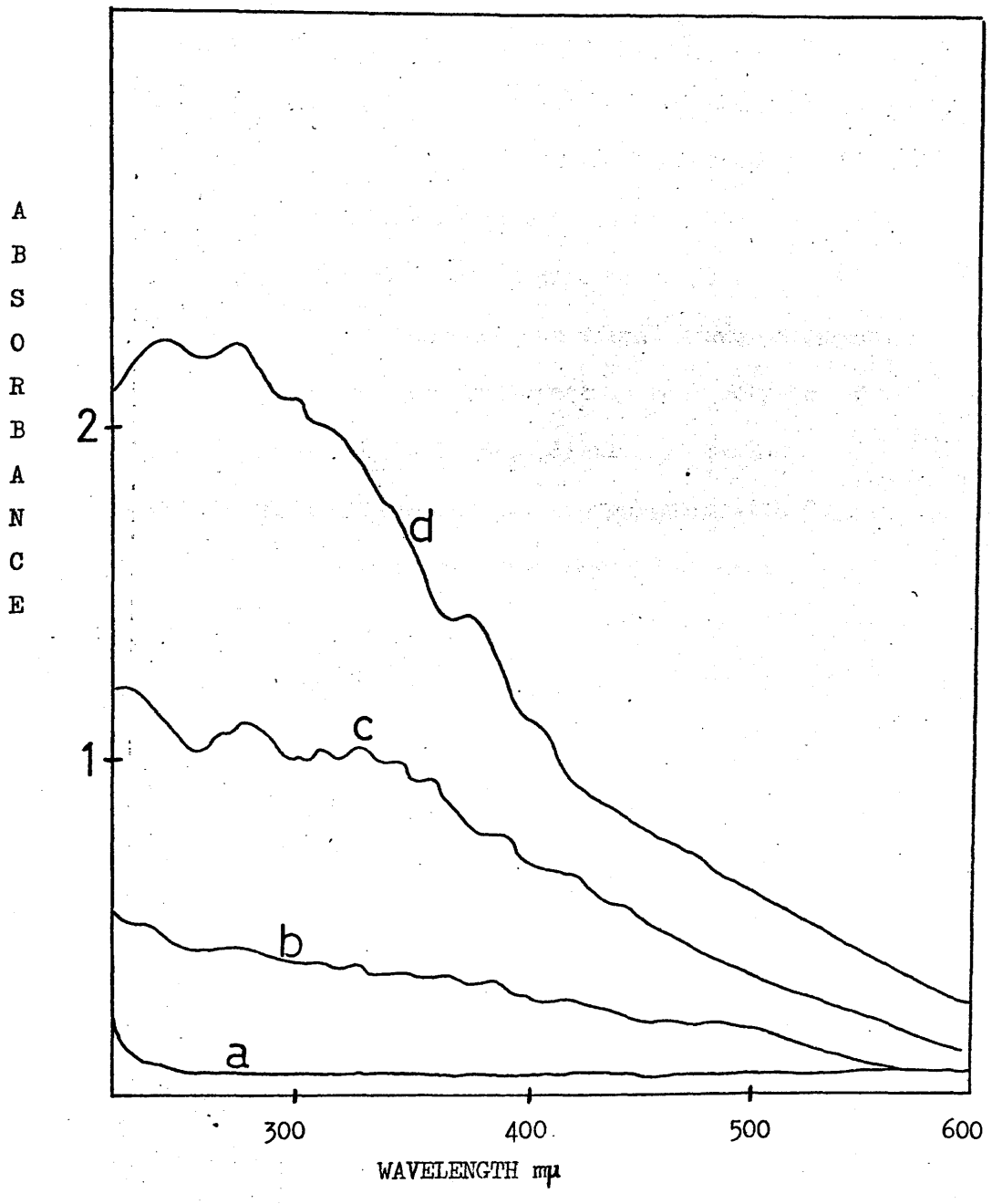
Fig 20

UV Spectra of 100mg film of head-to-head PVC



Head-to-head PVC undegraded (a) and heated at 10^0/min to 170^0(b) 180^0(c) 190^0(d)

Fig 21



UV Spectra of 100 mg. films of PVC Breon 113
Undegraded(a) and heated at 10^0/min to 215^0(b) 225^0(c) 250^0(d)

extends to 600mμ even in the early stages of degradation and as hydrogen chloride elimination proceeds, the intensity of absorption increases with the peaks at short wavelength growing most rapidly. This observation agrees with that of Thallmaier and Braun[53] and suggests that with increasing conversion the number of polyene sequences increases but their length does not. Peak maxima have been related to the degree of conjugation by several investigators[64-69]. Bengough and Varma[64] have assigned the peak at 475mμ in the degraded PVC spectrum to a polyene containing from 12 to 16 double bonds. Similarly, maxima between 285 and 365mμ have been assigned to polymers with 4, 5 and 6 double bonds in conjugation. From these figures it is evident that PVC Breon 113 forms polyene sequences ranging from 5 to at least 15 double bonds very early in the degradation process.

When the spectra of head-to-head PVC are compared with PVC Breon 113, the same general pattern is obvious, the only difference being that absorptions at higher wavelengths are neither as numerous nor as intense as PVC. Thus the head-to-head polymer also yields long polyene sequences on degradation. This confirms the visual observation that in the early stages of degradation, films of head-to-head PVC are reddish-brown and hence very similar in appearance to those of PVC.

EVOLUTION OF HYDROGEN CHLORIDE

The amount of hydrogen chloride liberated by head-to-head PVC was investigated using the product collection system of the TVA apparatus. Distilled water in a reservoir was frozen at-196°C and evacuated before degradation commenced. To estimate the hydrogen chloride liberated, the main trap and reservoir were sealed off and the hydrogen chloride was allowed to distil over into the reservoir which was subsequently sealed and allowed to thaw. Titrations were now carried out with standard 0.1M sodium hydroxide solution using phenolphthalein as indicator. To check the efficiency of the collection procedure samples of PVC Breon 113 were also degraded to the end of the dehydrochlorination stage. Since it is reported that at least 95% of the chlorine in PVC is eliminated as hydrogen chloride, the figure of 95.9% collected hydrogen chloride seems satisfactory. The results for head-to-head PVC are shown in Table 10.

TABLE 10

Temperature (°C)	Weight of sample (mgs.)	Volume of 0.1M NaOH (cm^3)	HCl as % polymer chlorine
271	101.6	1.15	10.4
282	101.1	2.70	24.1
301	100.4	3.70	33.6
325	101.0	6.75	61.0
352	100.8	8.30	74.8
379	101.4	10.10	91.1
396	101.2	10.70	97.0
498	100.9	10.70	97.1
PVC Breon 113			
410	102.5	10.80	95.9

At each temperature stated in Table 10, the experimental procedure was repeated. The titration figures given are the average value of the two titration figures obtained. The results show that head-to-head PVC loses approximately 95% of its chlorine as hydrogen chloride. Evolution of hydrogen chloride occurs mainly between 250° and 370° with the T_{max} value of 325°C corresponding to a 61.4% loss of chlorine as hydrogen chloride. Evolution of hydrogen chloride finally ceases at approximately 400°C.

KINETICS OF DEHYDROCHLORINATION

The kinetics of the dehydrochlorination reaction of head-to-head PVC were studied to determine the order of the reaction and also the value of the activation energy. It was hoped that if values could be calulated for these parameters, this would help to clarify the mechanism since differences in mechanism of degradation are reflected in very different values of activation energy. Chlorinated polypropylene which is thought to go by an ionic mechanism gives a value of approximately 8 Kcals/mole [70] while values of 24-36 Kcals/mole [71,72,73] have been reported for head-to-tail PVC which is thought by many people to degrade by a radical mechanism.

ACTIVATION ENERGY FROM A TG CURVE

Several methods are available for obtaining kinetic parameters from TG data[74,75,76]. The approach used in this case was that of Coats and Redfern[76]. Its advantages are that it is simple to use and holds for reactions of any order. The method involves plotting $\log \frac{Q}{T^2}$ against $1/T$ where $Q = \frac{1-F^{(1-n)}}{1-n}$ unless n = 1 where $Q = -\log F$.

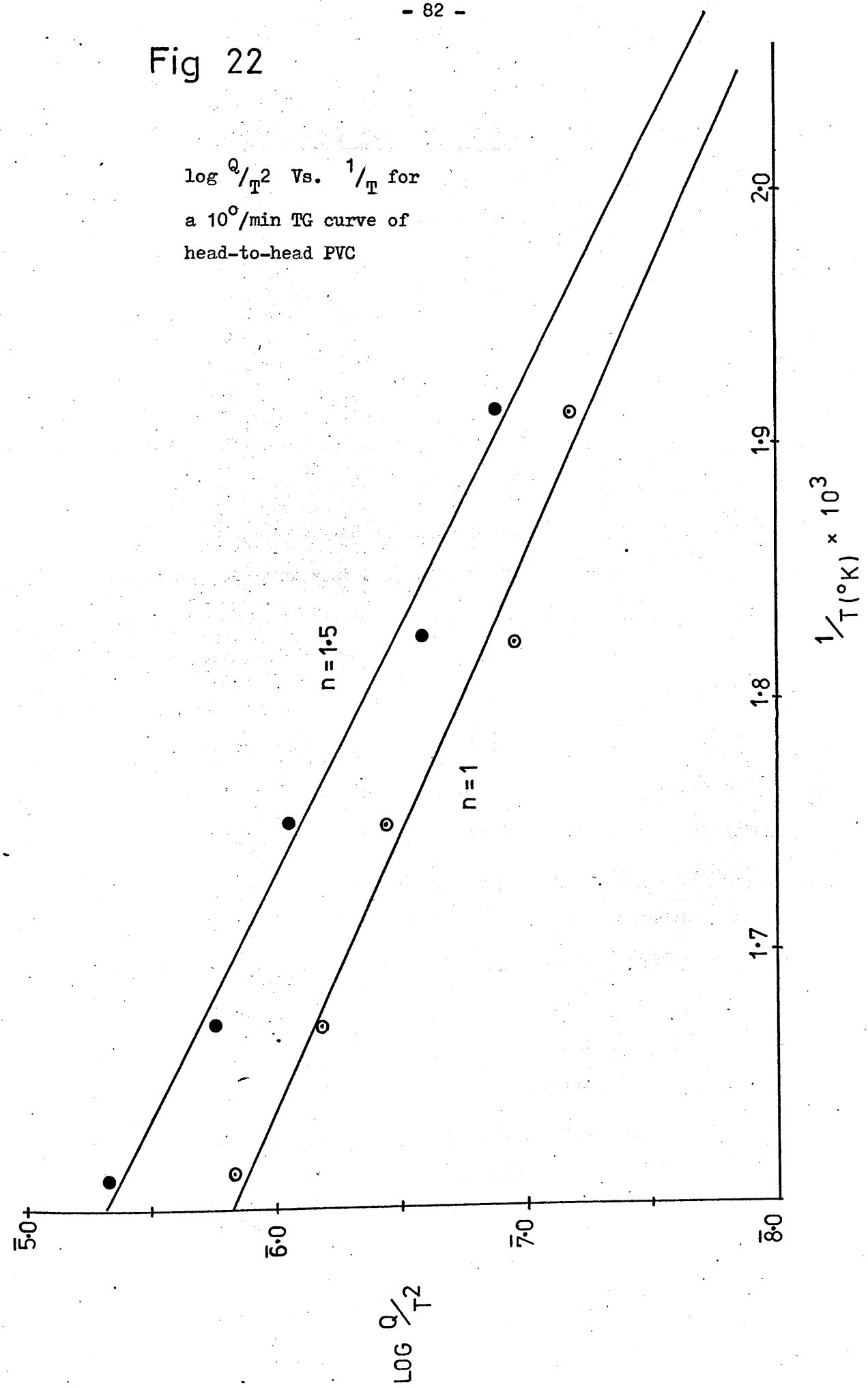
A full derivation of the above is given in Ref. 77. The best straight line is found by varying n and this line has the gradient $-E/2.3R$. The functions $\log Q/T^2$ with n = 1 and n = $3/2$ were calculated at temperatures 200, 225, 250, 275, 300, 325, 350 and 375°C. respectively and the graphs of $\log Q/T^2$ Vs $1/T$ obtained are shown in Fig. 22. One difficulty in applying this method to head-to-head PVC is the slight degree of overlap of the two stages of the TG curve. The end of the dehydrochlorination reaction was estimated as the point of inflection between the two stages and was more accurately determined using an expanded scale on both the weight and temperature axes. From the graphs it is evident that there is too much scatter in the results to decide which value of n produces the lesser curvature and accordingly the equations of the best fitting straight lines were calculated for both sets of points. The gradients of the lines were used to determine the activation energy

E_a = 21 Kcals/mole if n = 1

E_a = 24 Kcals/mole if n = $3/2$

Fig 22

$\log {}^{Q}/_{T^2}$ Vs. ${}^{1}/_{T}$ for a 10°/min TG curve of head-to-head PVC



KINETIC PARAMETERS FROM ISOTHERMAL TG DATA

Isothermal curves of the type shown in Fig. 23 were obtained at 200, 210. 225, 235 and 250°C respectively. The order of the reaction was found by two methods. Firstly, using the differential form of the rate equation the log (rate of reaction) was plotted against the log (% undegraded). The gradient of the straight line graph obtained gives a direct value of n the reaction order. The disadvantage of the method was that since rates of reaction were determined by drawing tangents to the TG curve, the accuracy of the method diminished at lower temperatures. Hence, while the isothermal TG curves at 225, 235 and 250°C gave fairly good straight lines, those at 200 and 210°C did not. The graph for T = 250°C is shown in Fig. 24 with the gradient giving a value of n = 1.52.

The other method used was to test for $^{3}/_{2}$ order by plotting (% undegraded) $^{-0.5}$ against time of degradation for the specific run. The graph was quite a good straight line as Fig. 25 shows, suggesting that 1.5 order kinetics are applicable. This method was applied to the isothermal curves, all of which showed straight lines except the 200° run which showed a slight degree of curvature. In order to determine the value of the activation energy, the log (initial rate of reaction) was plotted against the reciprocal of temperature. The initial rates of reaction were determined by plotting (%degradation) against time. The graphs are linear in the early stages of degradation. Initial rates were determined by measuring the gradient of the linear portion of the graphs. These values of initial rate were now plotted against $^{1}/_{T}$ and the graph obtained is shown in Fig. 26 The line has a gradient

Fig 23 Isothermal gravimetric curves of head-to-head PVC at (a) 200°C. (b) 225°C. (c) 250°C.

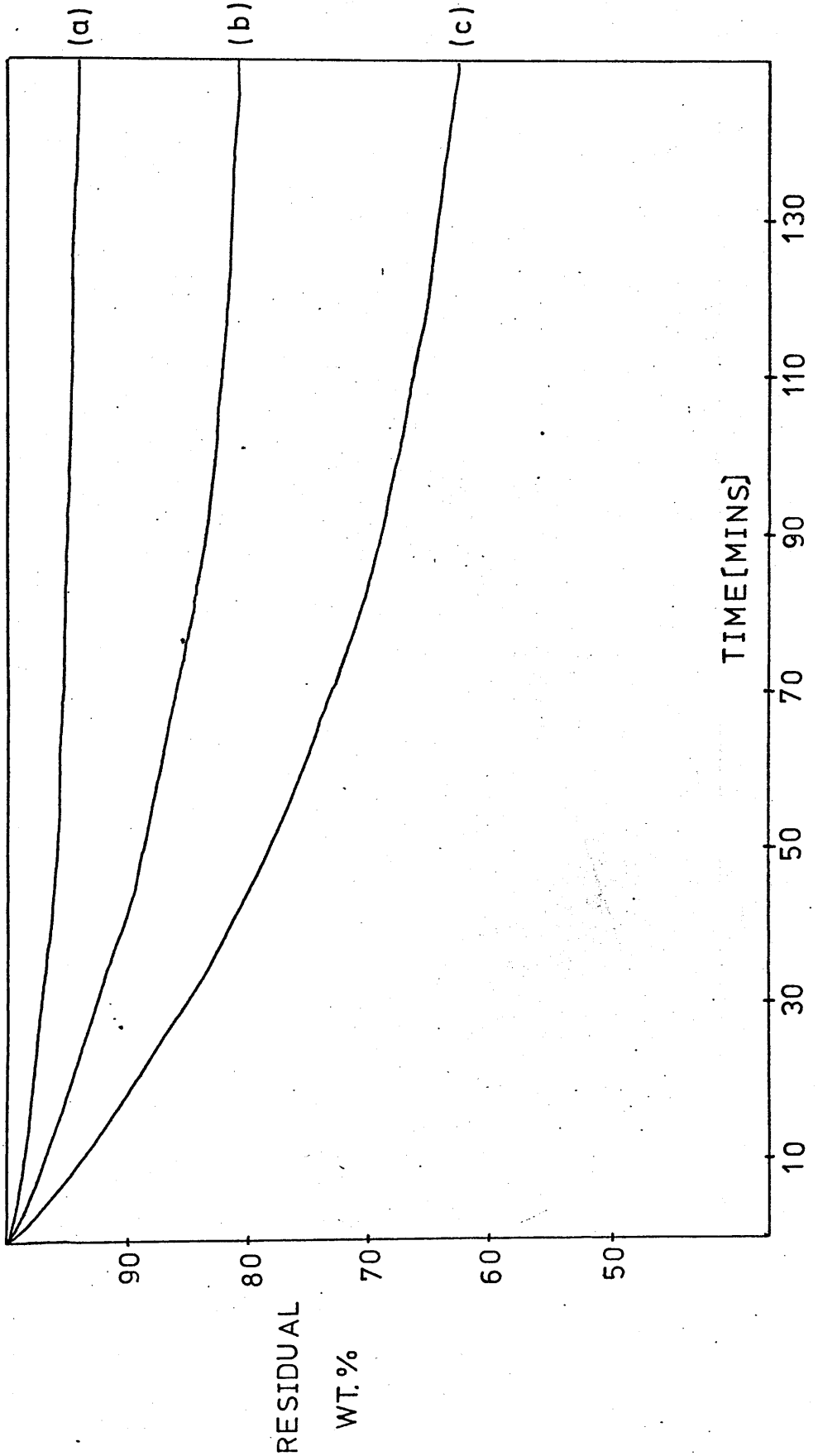


Fig 24

log(rate) Vs. log(% undegraded)
for head-to-head PVC.
Isothermal degradation at 250°C.

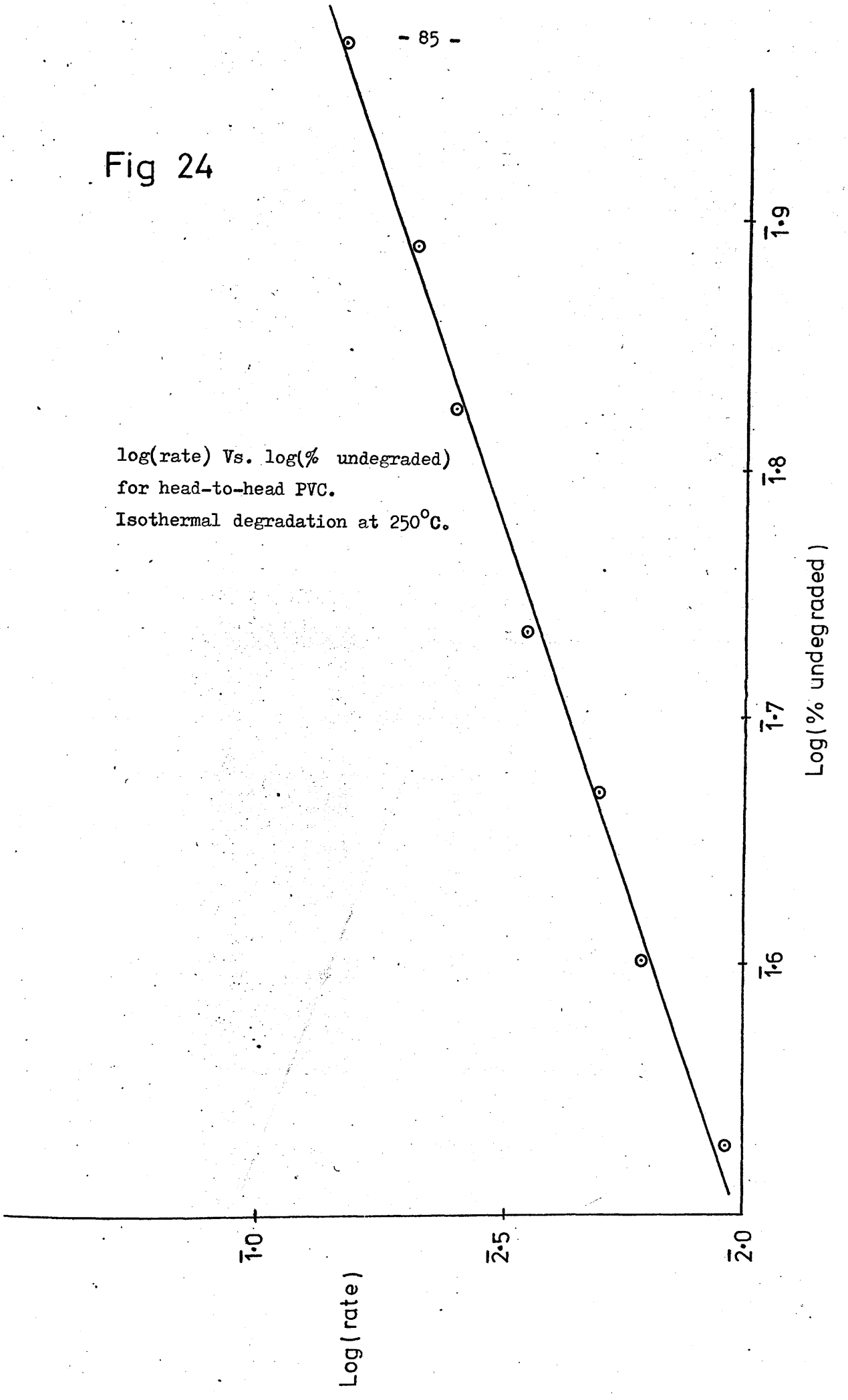


Fig 26

log(rate) Vs. $^{1}/_{T}$ for head-to-head PVC isothermal degradations

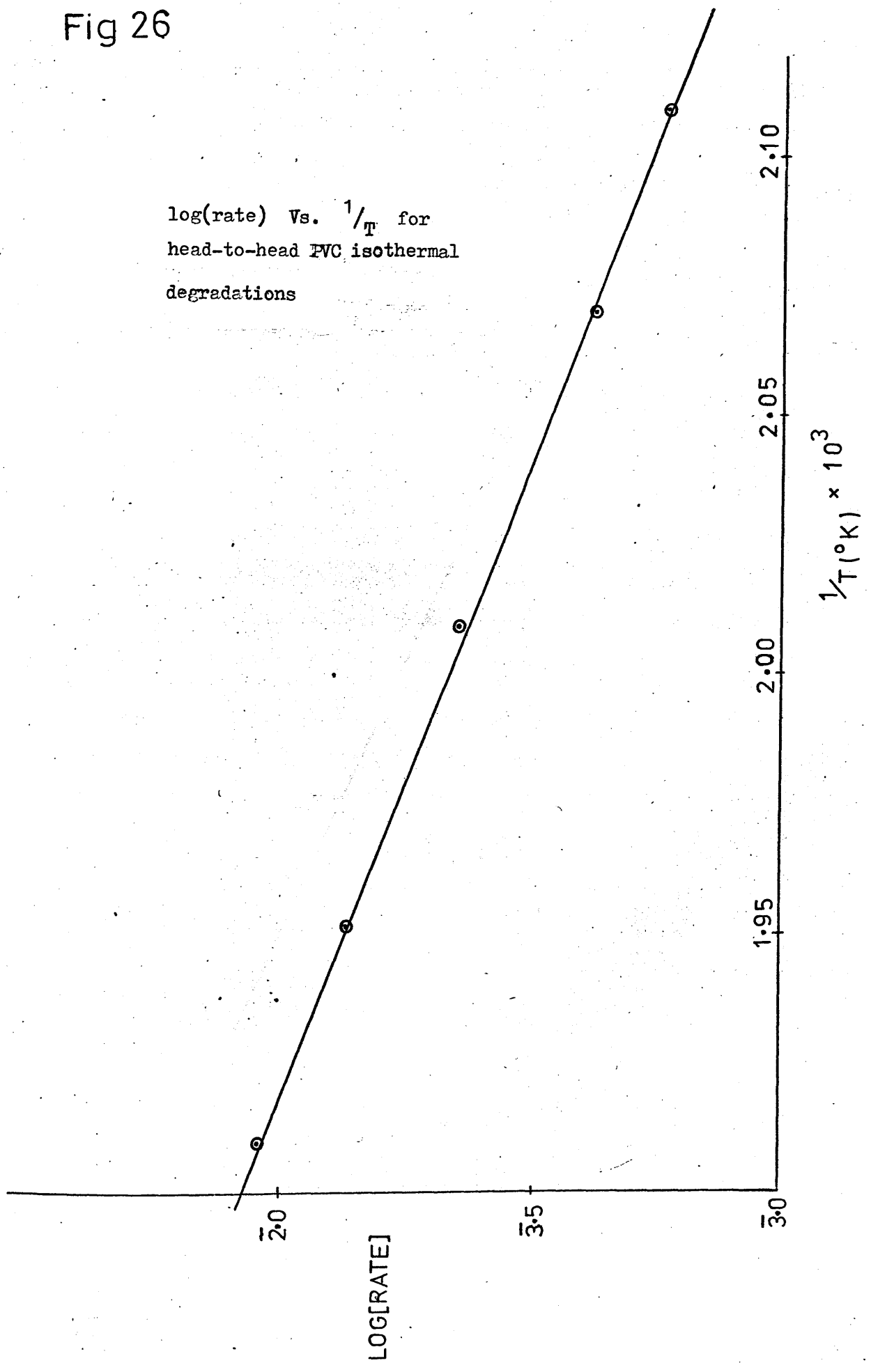
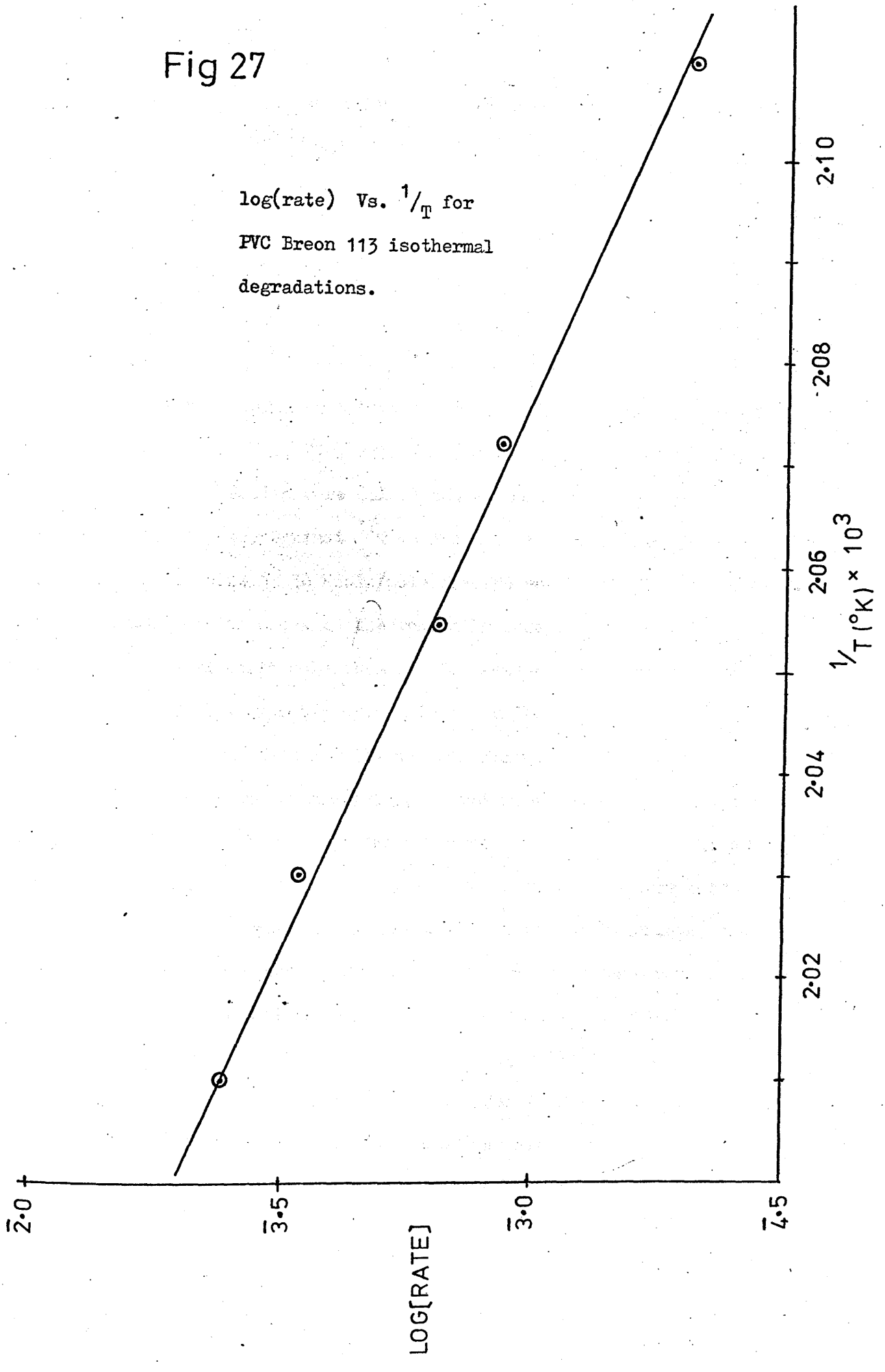


Fig 27

log(rate) Vs. $^{1}/_{T}$ for PVC Breon 113 isothermal degradations.

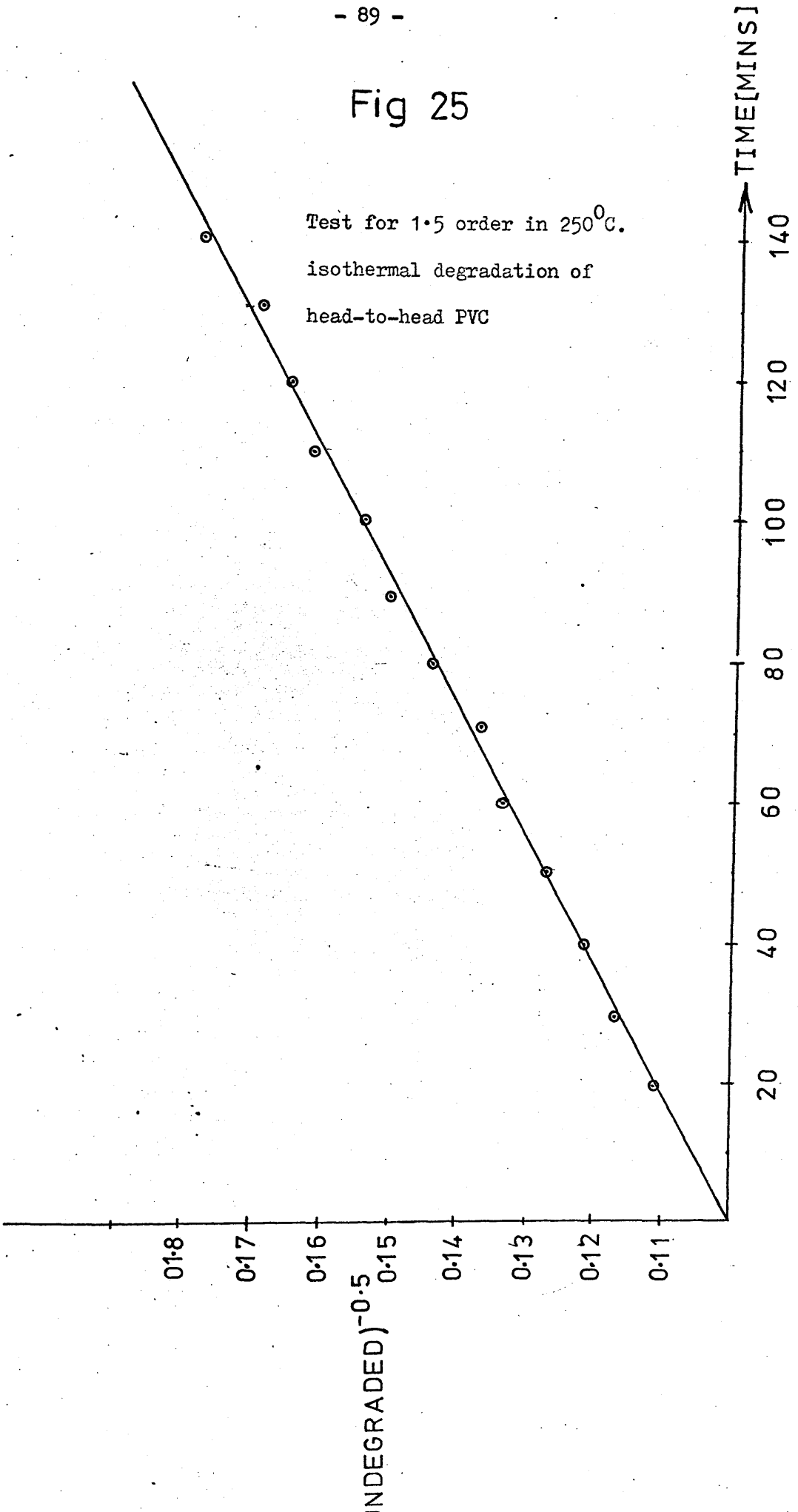


$-E/2.3R$ and the value of the activation energy was 21 Kcals/mole. Since the value of the energy of activation may vary greatly depending on the experimental method used, it was necessary to check the values obtained by determining the value of the activation energy of the dehydrochlorination reaction of head-to-tail PVC which is generally accepted as having a value about 30 Kcals/mole.[75,76,77]

Isothermal gravimetric curves were obtained for samples of PVC Breon 113 at 200, 210, 215, 220 and 225°C respectively. Initial rates of reaction were calculated as before and the graph of log (initial rate) against $1/T$ is shown in Fig. 27. The gradient gives a value of 38 Kcals/mole for the energy of activation. Since this is close to the generally accepted value, the figure of 18 - 24 Kcals/mole obtained for head—to-head PVC is assumed to be of the expected order of magnitude.

One factor which may influence the accuracy of isothermal results obtained by thermogravimetry, is the rate at which the polymer sample reaches the required isothermal temperature. In order to minimise temperature lag, smaller sample sizes were used and spread thinly over the sample pan. Using this technique, the polymer sample appeared to reach the required temperature within a very short time of its introduction into the oven, while the kinetic data obtained was always reproducible for a number of runs at the same temperature. In order to check the accuracy of this method, an alternative method was also used. This involved placing the sample in the oven initially and heating to the

Fig 25


Test for 1·5 order in 250°C.
isothermal degradation of
head-to-head PVC
TIME[MINS]
20
40
60
80
100
120
140
UNDEGRADED)$^{-0.5}$
0·18
0·17
0·16
0·15
0·14
0·13
0·12
0·11

required isothermal temperature. Values of activation energy and reaction order calculated by this method were always identical to those obtained by the first method.

ACTIVATION ENERGY FROM HCl EVOLUTION DATA

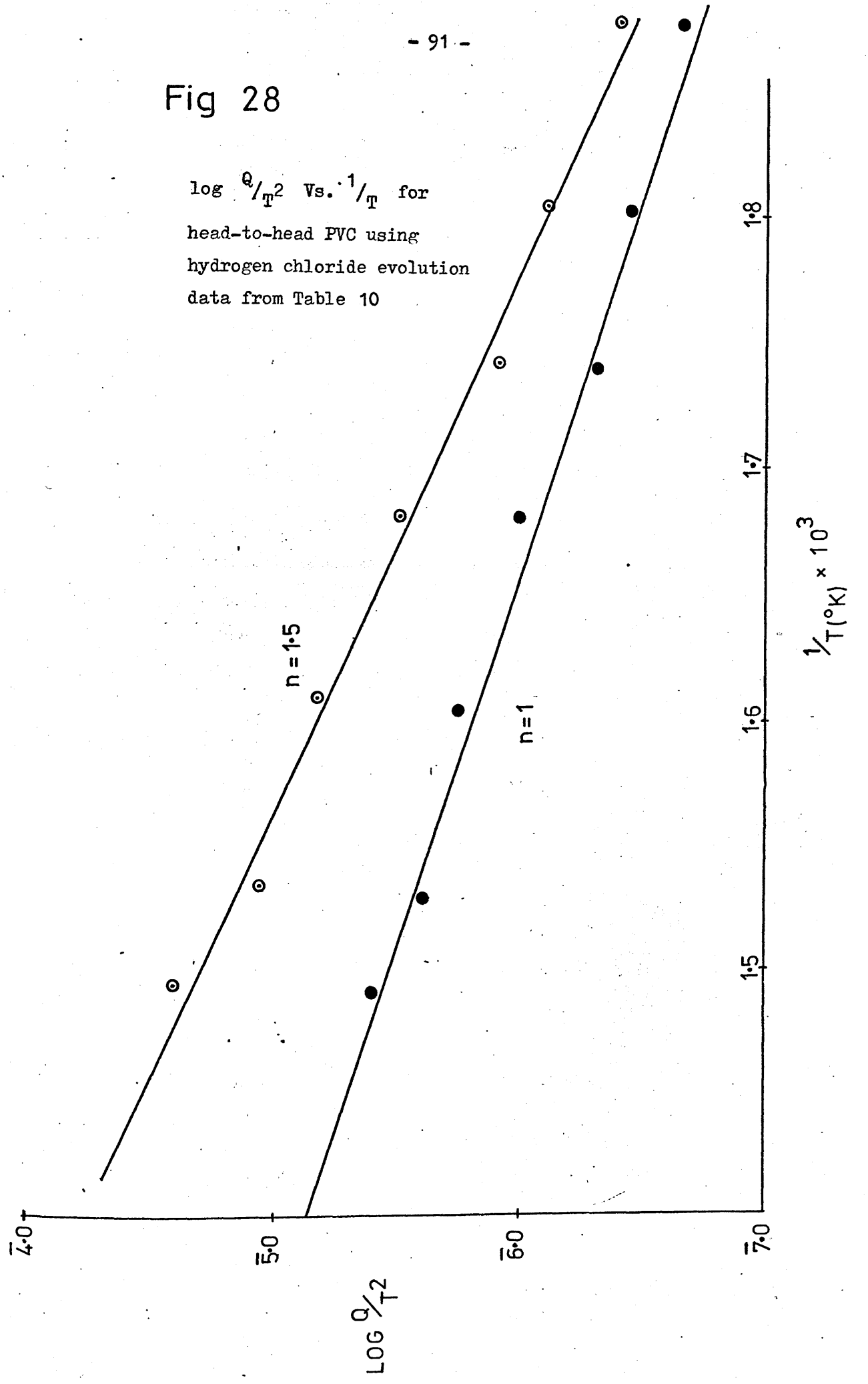
Coats and Redfern's method was applied to the dehydrochlorination reaction of head-to-head PVC using the data in Table 10. The value of F was taken as (1 - fraction of polymer chlorine lost as hydrogen chloride). This is valid even in the presence of side reactions provided they do not remove chlorine. Since the polymer loses approximately 95% by weight of its chlorine as hydrogen chloride, it follows that any errors due to competing side reactions removing chlorine would be fairly small. The calculation was performed for the mean results at the following temperatures 271, 282, 301, 352, 379, 395 and 498°C respectively for values of n = 1 and n = $^{3}/_{2}$. The graphs produced are shown in Fig. 28. There is again too much scatter in the results to decide which value of n produces the lesser curvature and accordingly the equations of the best fitting straight lines were calculated for both sets of points. The gradients of the lines were used to determine the activation energy which was found to be

E = 18 Kcals/mole if n = 1

E = 21 Kcals/mole if n = 1.5

Fig 28

log Q/T^2 Vs. $1/T$ for head-to-head PVC using hydrogen chloride evolution data from Table 10

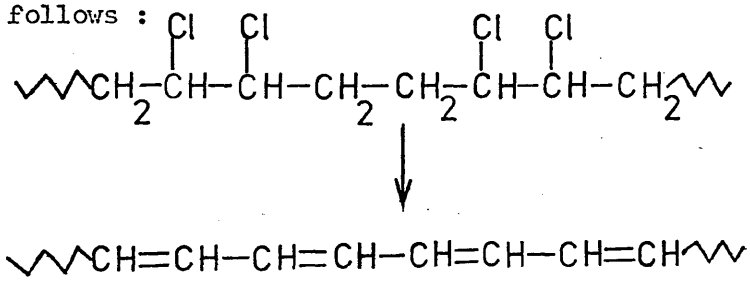


SUMMARY

Isothermal degradations using thermogravimetric techniques in the temperature range 200° - 250° gives a value of 21 Kcals/mole Treatment of the results from programmed experiments using the temperature range 20° - 500° gives values from 18-24 Kcals/mole. Hence the value of energy of activation obtained from isothermal and temperature programmed experiments are closely similar. Values of n = 1 and n = 1.5 were both found to fit the data from programmed degradation experiments whereas for most isothermal data a value of n = 1.5 was found to be most satisfactory.

CONCLUSION

Thermal analysis shows that degradation of head-to-head PVC occurs by hydrogen chloride elimination. Although TVA shows only one peak corresponding to the dehydrochlorination reaction, this peak is fairly broad in appearance and hence the possibility of more than one type of process occurring must be considered. TVA and TG show that secondary decomposition of the backbone begins shortly before elimination is complete. Despite this small degree of overlap, product analysis shows that the yield of chlorine as hydrogen chloride is virtually quantitative. Examination by UV spectroscopy shows the presence of fairly long polyene sequences even in the very early stages of degradation. The mechanism of degradation may be respresented as follows :



It is useful to examine at this stage any evidence which might suggest whether the mechanism is essentially radical, ionic or unimolecular in nature.

Since the polymer rapidly becomes insoluble on heating, some degree of cross-linking is occurring. Although this process is often radical in nature, it may also be of the Diels-Alder type and hence this in itself is not sufficient evidence for a radical mechanism. Analysis of the kinetic data shows that the reaction

has an activation energy of about 20 Kcals/mole, which is much lower than might be expected for unimolecular elimination of hydrogen chloride but consistent with a radical chain process. From programmed degradation results it is difficult to give the reaction a specific order since both n = 1 and n = 1.5 fit the data. However, for most isothermal runs, a value of n = 1.5 was found to fit the data. This value has also been found for head-to-tail PVC degradation and is typical of many radical chain reactions. Therefore kinetic studies tend to suggest a radical type process. In order to obtain more evidence, thermal studies were extended to cover polymer blends as described in Chapter 5.

CHAPTER 5

POLYMER BLENDS

(A) Blends of head-to-head PVC with poly(methyl methacrylate)

Introduction

The blending of one polymer with another can often be used to modify the properties of the polymer and extend its applications.[84] Commercial use is made of this in order to obtain polymers with enhanced physical properties. The study of polymer blends has shown that the degradation behaviour of one polymer is often affected by intimate contact with another.[37, 85, 86, 87]

Unlike macromolecules are, in general, incompatible in the solid state,[29,30,31] so that the method used of casting them together as a film from a common solvent, usually results in a heterophase which, at best consists of domains or micelles of one polymer in a continuous matrix of the other. Thus, a polymer blend is neither a true mixture, nor a solid solution. During pyrolysis of a polymer blend, therefore, any interaction between the components (or with the products of degradation) must occur at phase boundaries or, by the diffusion of small molecules into the second phase. Unless the reaction environment is one of a polymer melt, the second of these possibilities will be severely restricted. McNeill and Neil [37,88] have shown that the degradation

pattern of PMMA is markedly different when PVC is also present, and have cited this as evidence for the existence of small radical species, and hence for a radical mechanism for the degradation of PVC. This system will be discussed in greater detail later. A study of polymer blends, therefore can be of considerable importance in classifying the mechanism of polymer degradation. In the preceding chapter, the thermal degradation of head-to-head PVC was discussed in some detail. In the work described in this chapter, the objective was to obtain further information on the degradation behaviour of head-to-head PVC by degrading blends of head-to-head PVC with PMMA in experiments similar to those performed by McNeill and Neil [37,88]. In order to make a valid comparison, the experiments of McNeill and Neil were repeated and the results recorded. Before studying the behaviour of head-to-head PVC in blends, it is worthwhile to discuss further the experimental results and conclusions of the above authors.

Degradation of PVC/PMMA Blend Systems

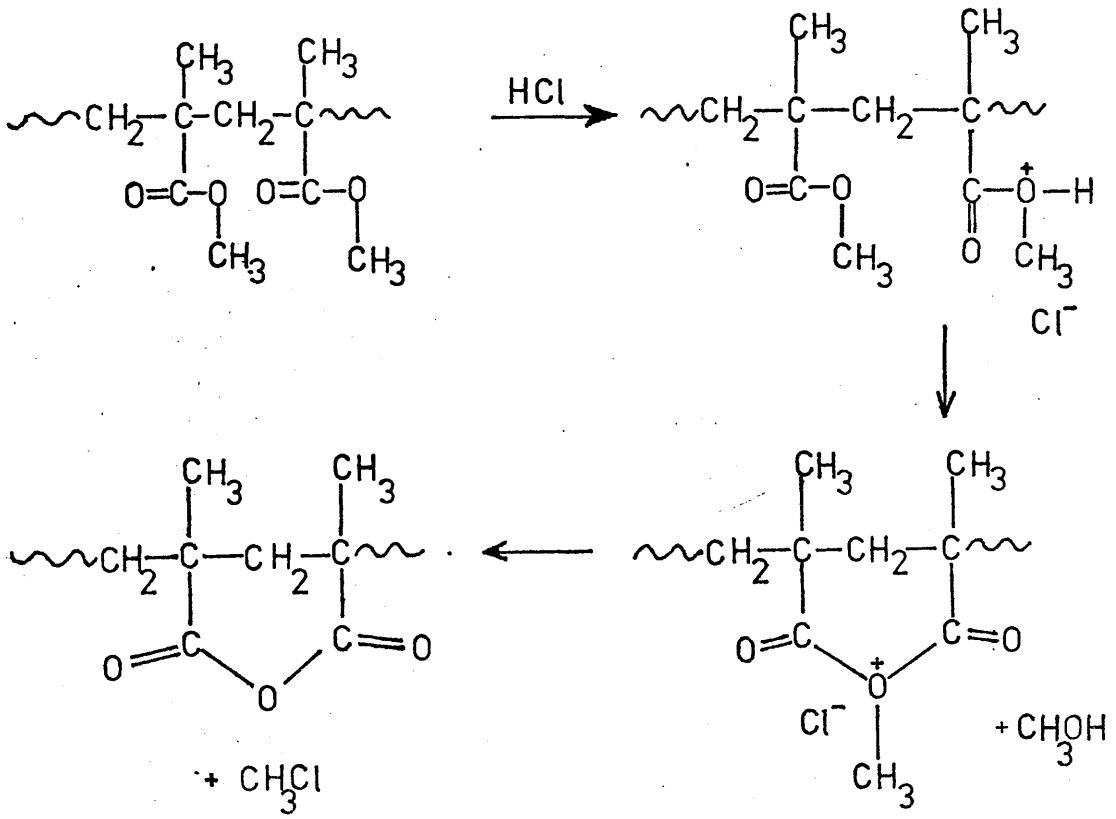
This heterogeneous system was extensively studied by the authors [37,88] who found that when PVC, was degraded in the presence of PMMA using the technique of differential condensation TVA, the production of methyl methacrylate monomer was greatly enhanced in the early stages of degradation while the evolution of hydrogen chloride from PVC was retarded slightly. In addition small amounts of non condensable material were evolved during

the later part of degradation while the peak maximum temperature for methyl methacrylate production was delayed. The conclusions that they drew from these results were as follows:-

1. Chlorine atoms diffuse from the degrading PVC into the regions in the blend which contain PMMA. Once there, these small radicals initiate depolymerisation reactions in PMMA chains.

2. PVC degradation is consequently retarded, since chain-propagating atoms are lost by diffusion into PMMA regions.

3. Interaction also takes place between the hydrogen chloride evolved and the PMMA chains. PMMA is stabilised in this reaction by the formation of anhydride units. It is these anhydride units which break down at higher temperatures to give small amounts of non-condensable products. The mechanism of this process is shown below.



These authors have subsequently used the destabilisation effect noted under the first heading as a criterion for the presence of small radicals in the degradation of a particular polymer; i.e. if a blend of a particular polymer with PMMA causes earlier production of methyl methacrylate monomer during the thermal degradation, then this is taken as evidence for the presence of small radicals.

McNeill and Gardner[65] used this criterion in their study of polychloroprene degradation. Although polychloroprene eliminates hydrogen chloride on degradation, when degraded in the presence of PMMA no increase in methyl methacrylate production was observed. The authors concluded, therefore, that no small radicals were produced in degrading polychloroprene.

The degradation of blends of head-to-head PVC with PMMA was therefore studied with special regard to whether or not increased production of methyl methacrylate occurred, thus providing evidence for or against the presence of small radicals in the degradation of head-to-head PVC.

Degradation of blends of Head-to-head PVC with PMMA

Evidence from differential condensation TVA

The polymers were studied using the twin-limbed 'trouser' tube which has been described previously in Chapter 2. Blends were studied in the form of thin films cast on the base of the tube as previously described, or as finely ground powders.

PMMA degrades completely to monomer by two possible reaction mechanisms.[89-95] In the first, depolymerisation is initiated at unsaturated chain-ends, and in the second, the depolymerisation reaction proceeds after random scission of the polymer backbone. Thus PMMA prepared by a free radical process has two peaks in the TVA curve. The lower temperature peak is due to the first reaction, and the peak size is proportional to the number of chain-ends which the polymer contains. High molecular weight PMMA shows no peak for chain-end initiations. For simplicity, this type of PMMA was used in the investigation.

In the differential condensation TVA curve, methyl methacrylate from PMMA degradation is trapped at -75°C. but not fully condensed, since it distils away at a constant rate to give a characteristic plateau effect[96] which has been described previously on Page 21. Methyl methacrylate monomer is completely condensed at temperatures of -100°C. or lower.

The differential condensation TVA curve for PMMA is shown in Fig. 29 while that for head-to-head PVC is shown in Fig.11. The curve for PMMA consists of a single peak with T_{max} corresponding to 390°C. The curve for a 1:1 blend of PMMA and head-to-head PVC is shown in Fig. 30 while that obtained for equal amounts of the unmixed polymers is shown in Fig. 31. It can be seen that the first peak in the 'unmixed' sample is due almost entirely to material which is not condensed at -100°C., and corresponds to the dehydrochlorination of head-to-head PVC. The second peak consists mainly of material condensed at -100°C. and giving the characteristic limiting rate effect in the -75° trace, confirming this to be methyl methacrylate monomer.

For the mixed sample, in Fig. 30, the first peak is considerably altered in shape. The peak is much broader in appearance, and the 0°, -45°, -75° and -100°C traces are no longer coincident. On the low temperature side of the peak, material is being produced which is non-condensable at -45°C and gives a limiting rate in the -75° trace.

Subsequent analysis by gas-liquid chromatography confirmed that this was methyl methacrylate. The second peak also undergoes a considerable change in appearance. The peak is smaller and flatter and the T_{max} value has moved to a higher temperature (420°C). The production of hydrogen chloride from the mixed film appears to be more or less unaltered since the position of the T_{max} for hydrogen

Fig 29

Differential Condensation TVA curve for 20 mg. film sample of high molecular weight PMMA

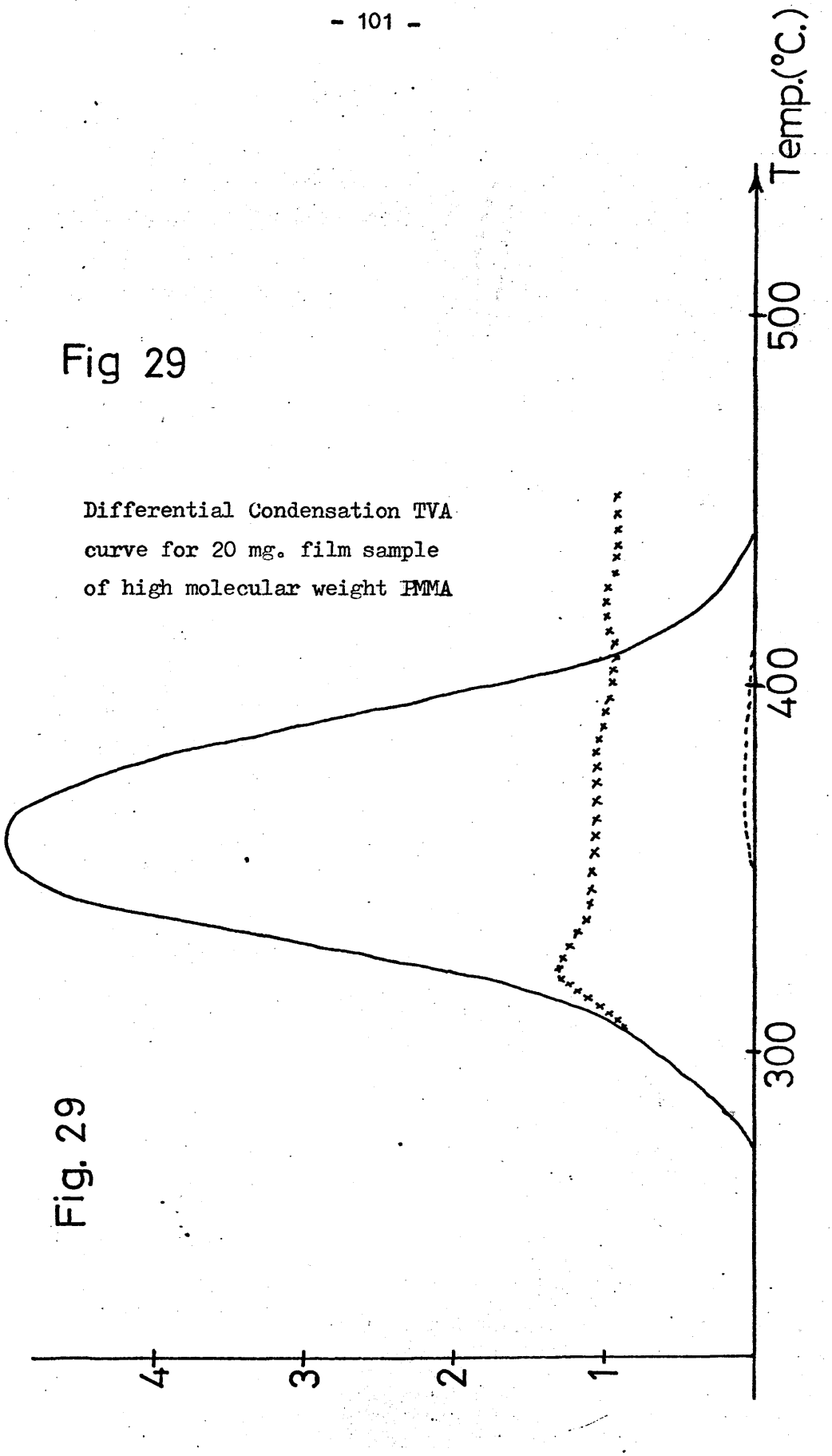


Fig. 29

Fig 30

DC-TVA curve for simultaneous degradation of head-to-head PVC and PMMA, 20 mg. each. Film samples - MIXED

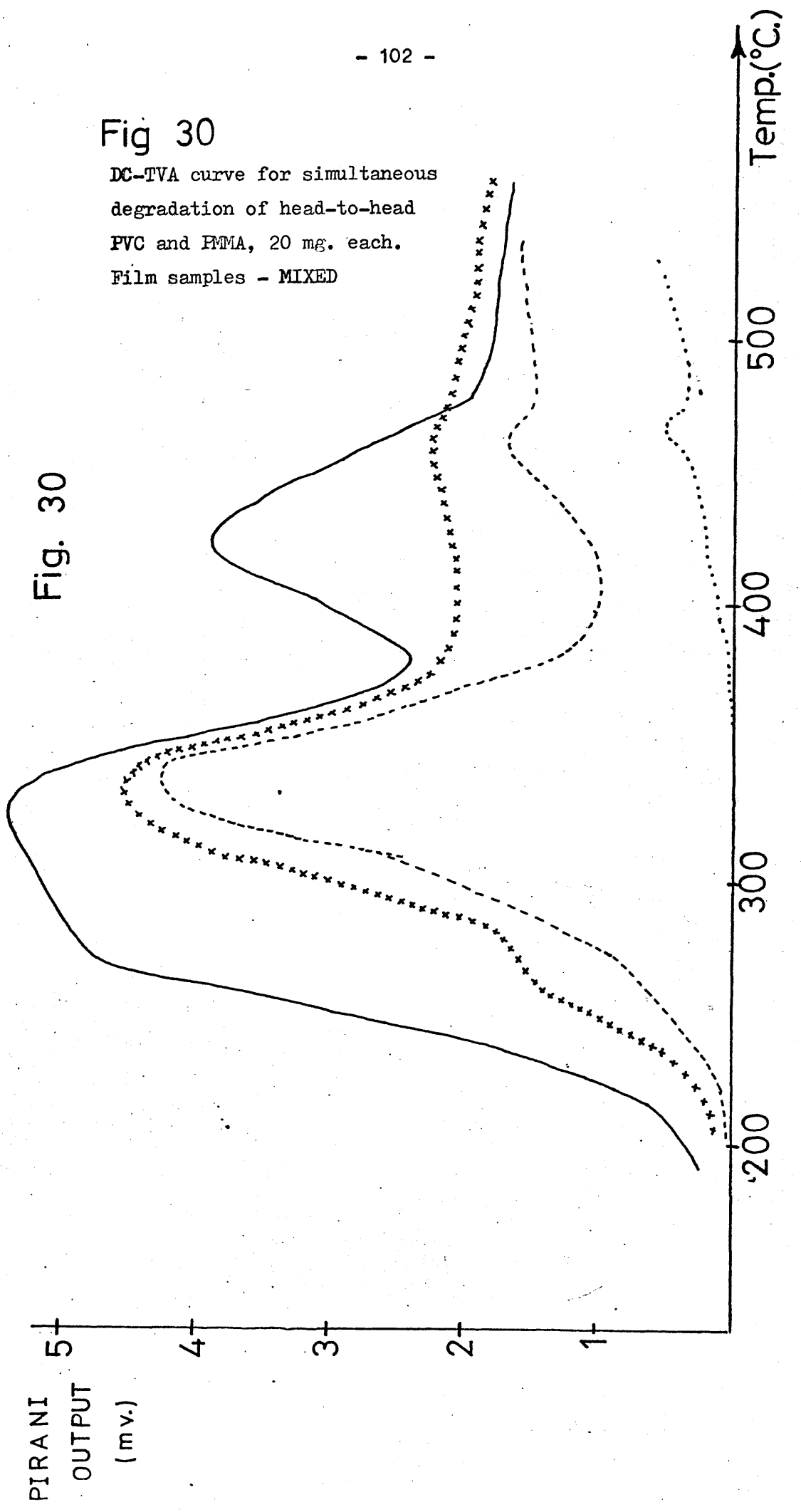
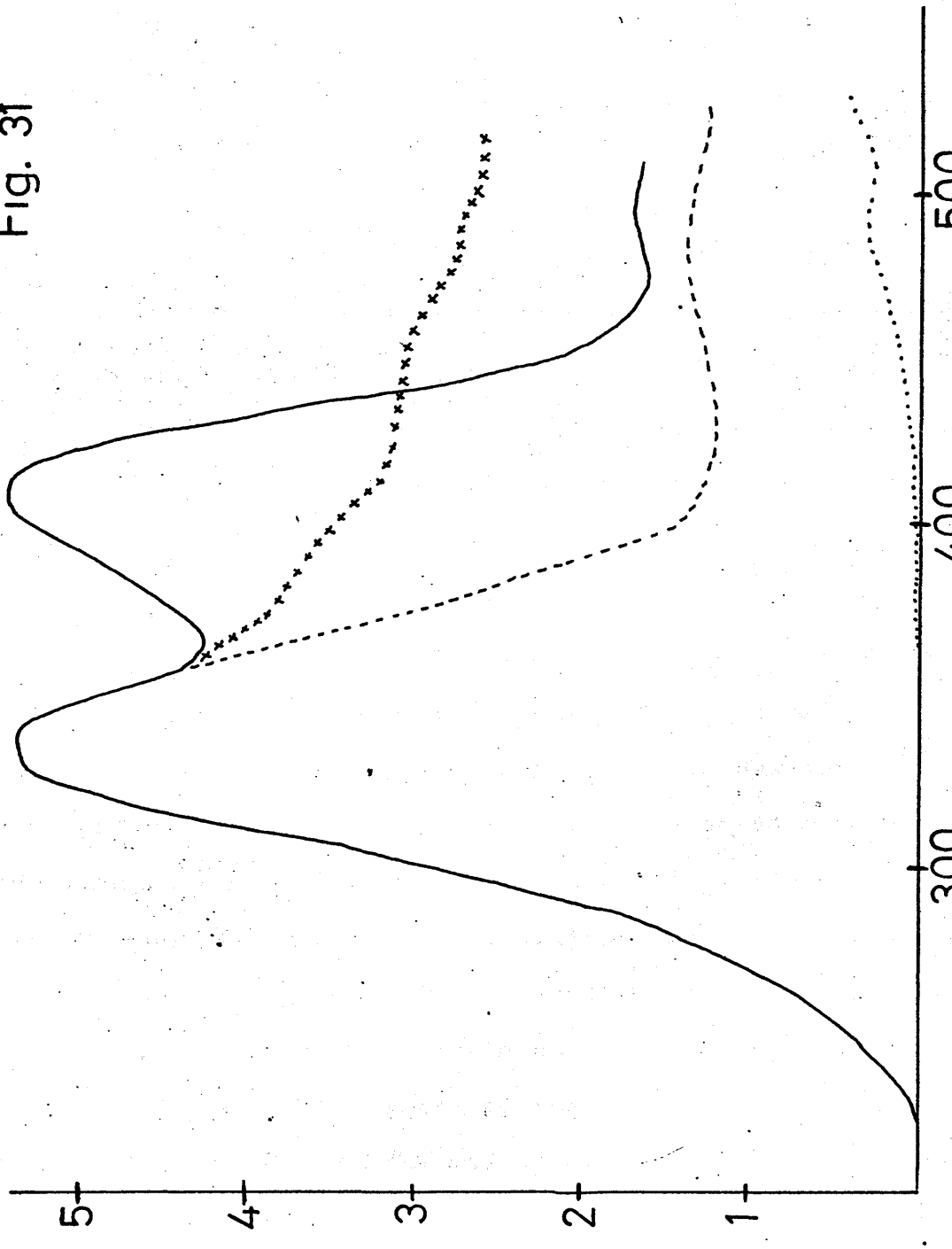


Fig. 30

Differential Condensation TVA curve for simultaneous degradation of head-to-head PVC and PMMA, 20 mg. each: Film samples. - UNMIXED

Fig. 31



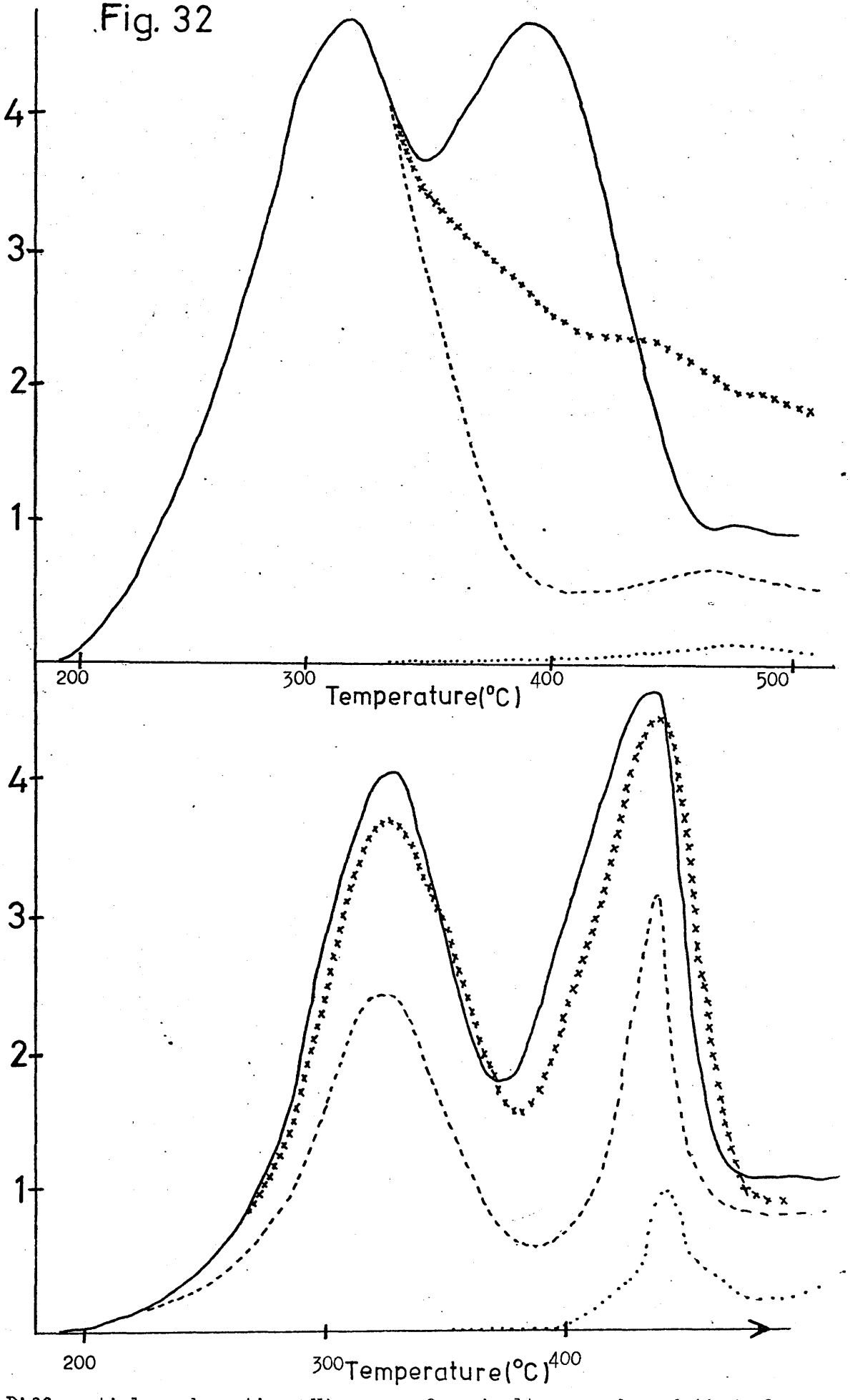
chloride production is unchanged. A further difference in the mixed system is that slightly more non-condensable material is evolved in the later stages of degradation.

Differential Condensation TVA - Studies of powder blends

PMMA/Head-to-head PVC

Samples of head-to-head PVC and PMMA were ground to fine powders capable of being passed through a 0.0049 inch mesh. A blend of the two polymers was obtained by placing equal weights of the two powders in the same container and stirring for one hour. Differential condensation TVA curves were obtained for the degradation of equal weights of the two polymers in the mixed and unmixed condition, using the same twin-limbed trouser-tube as before. The curves obtained are shown in Fig. 32. Again there is evidence of interaction between the two polymers. This time there appears to be a larger increase in the amount of non-condensable material produced in the later stages of degradation. However, there appears to be little evidence for increased monomer production in the early stages of degradation. Separation of the 0^{o} and -45^{o} traces is not distinct as in the case of the film blends. The increased production of non-condensable material at high temperatures can be explained by the longer retention of hydrogen chloride by the thicker powder samples Stabilisation of the PMMA chains by reaction with hydrogen chloride, thus occurs to a greater extent and therefore

Fig. 32



Differential condensation TVA curves for simultaneous degradation of head to head PVC and PVAc 20 ... of each powder samples

breakdown at higher temperature increases.

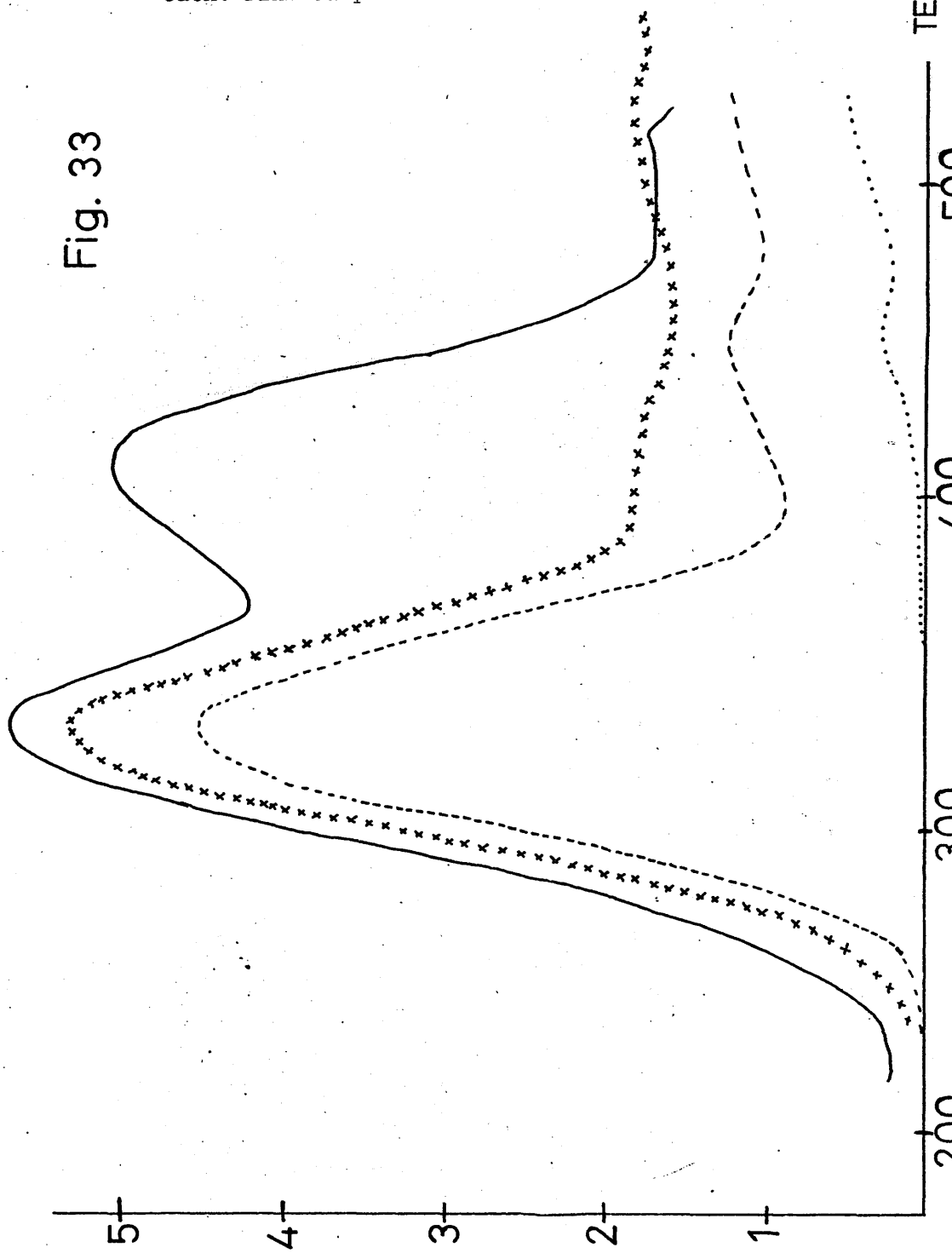
TVA studies of blends of PMMA with PVC Breon 113

Similar experiments were also carried out using blends of PMMA with PVC Breon 113. The differential condensation TVA curve for Breon 113 is shown in Fig. 15 and has been discussed previously in Chapter 4. For powder samples or for films of more than 2.5mg/c.c., a curve of the type (A) is obtained, with the main peak being consistent with the dehydrochlorination reaction,[97] whereas for thin film samples, the T_{max} of this peak is moved to higher temperatures. The reason for this is that hydrogen chloride diffusing through the sample can cause autocatalysis, and therefore thicker samples which hinder diffusion are less stable. The differential condensation TVA curves for mixed and unmixed film samples are shown in Fig.33 and 34. The curves for the unmixed film samples consist of two slightly overlapping peaks, the first at lower temperature corresponding to the hydrogen chloride evolution from the PVC Breon 113 (non-condensable at -100°C), while the second peak at higher temperature shows material giving a limiting rate at -75°C and corresponds to methyl methacrylate. For the mixed sample there is considerable evidence for interaction between the polymers.

Firstly, the peak at lower temperature is increased in height and indicates the presence of material which is condensed at -100°C and shows a limiting rate in the -75°C trace (methyl methacrylate). Secondly evolution of hydrogen chloride is

Differential Condensation TVA curve for simultaneous degradation of PVC Breon 113 and PMMA, 20 mg. each: Film samples - MIXED

Fig. 33



Differential Condensation TVA curve for simultaneous degradation of PVC Breon 113 and PMMA, 20 mg. each: Film samples - UNMIXED

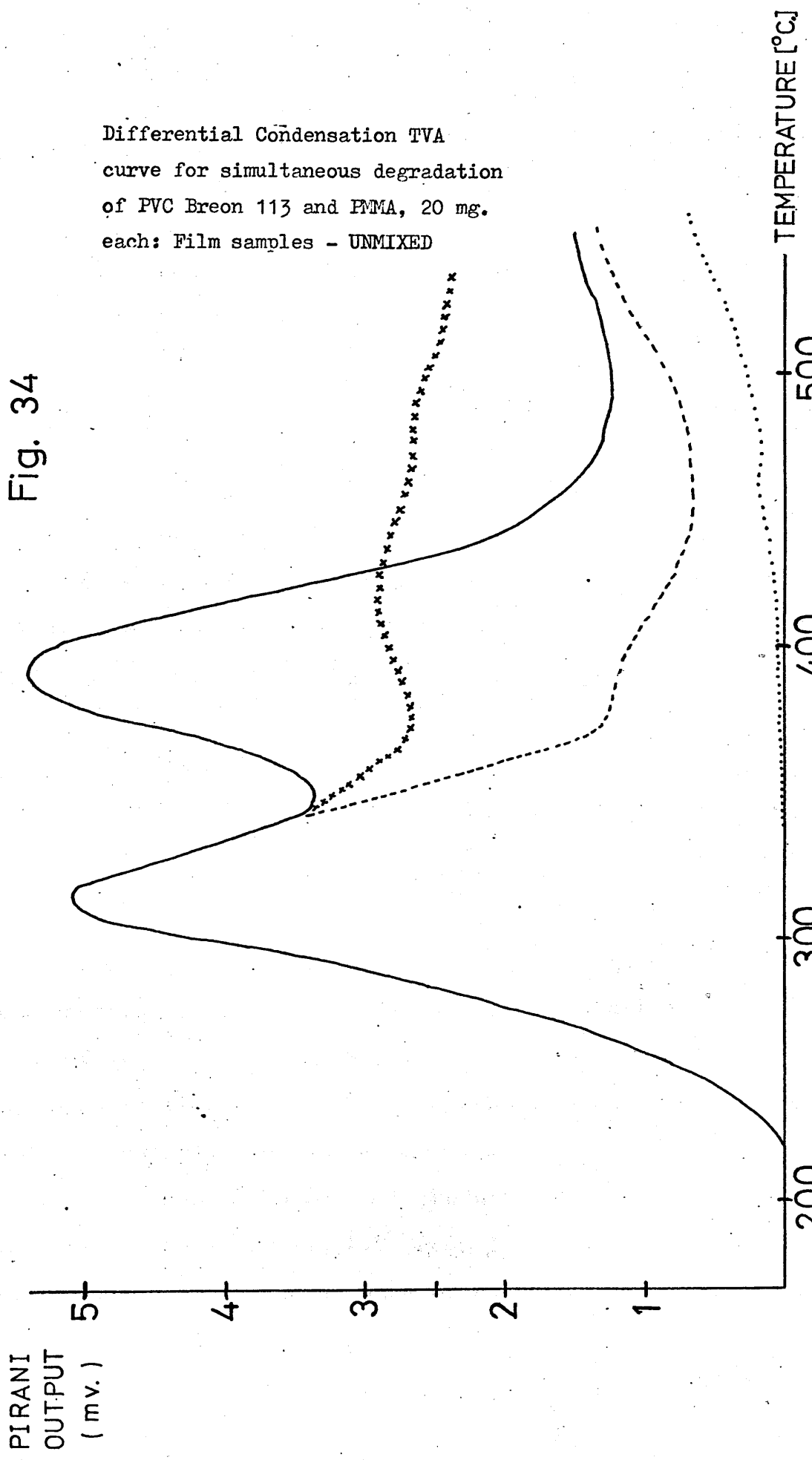


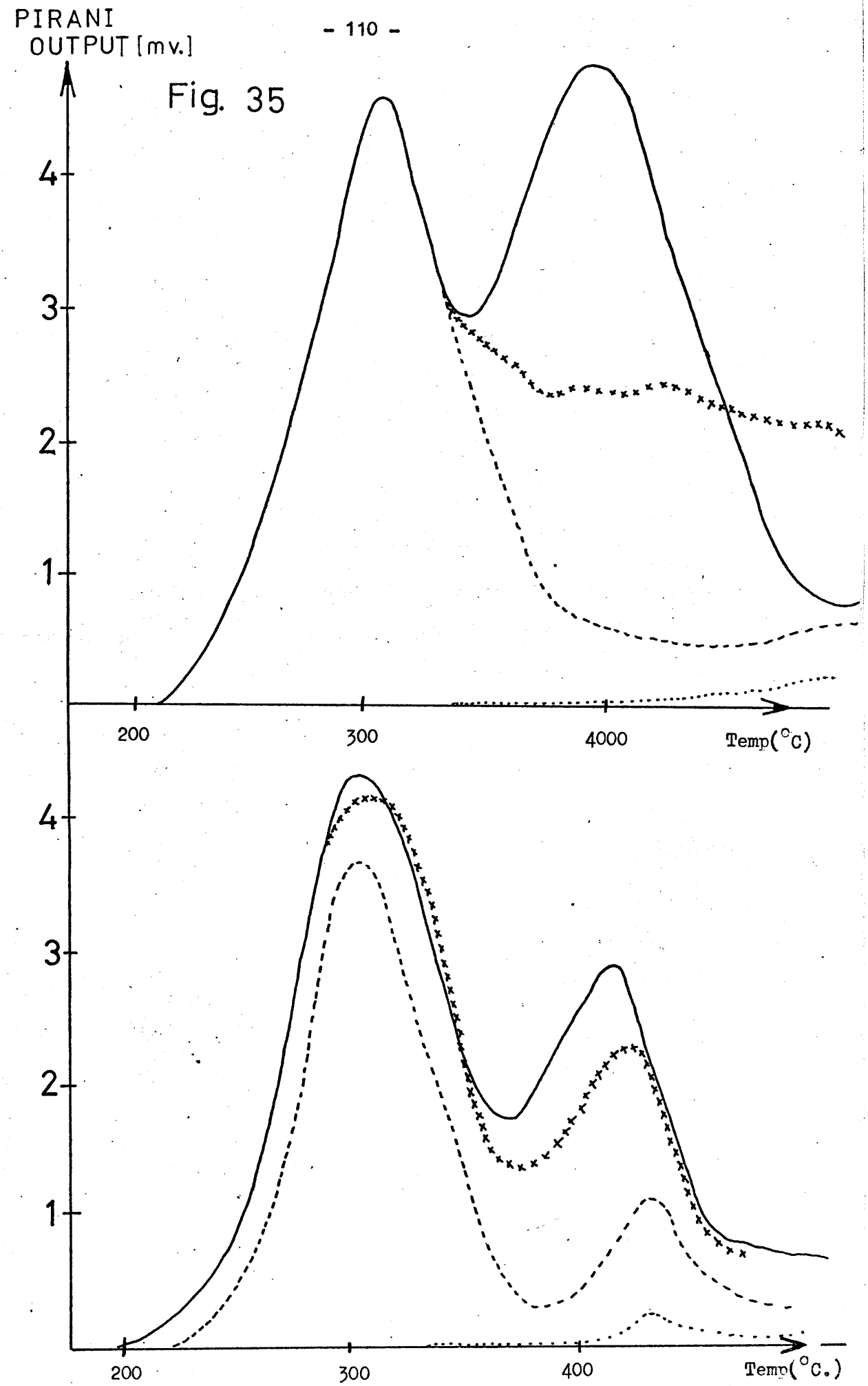
Fig. 34

retarded with the peak maximum moving from 310° to 325°C. Thirdly, the second peak consistent with evolution of methyl methacrylate is moved to higher temperatures with a corresponding increase in the amount of non-condensable material. These results were essentially the same as those obtained by McNeill and Neil[37,88].

Studies of Powder Blends

PMMA/PVC Breon 113

Powder samples of Breon 113 and PMMA were finely ground and mixed as previously described. The differential condensation TVA curves for the mixed and unmixed samples are shown in Fig. 35. As in the case of head-to-head PVC, the evidence for increased monomer production is not clearly obvious, although there is again a significant increase in the amount of non-condensable material in the later stages of degradation, caused by the action of hydrogen chloride on the ester groups of PMMA. When the behaviour of head-to-head PVC and head-to-tail PVC with PMMA is compared, it can be seen that the interactions in each case are virtually identical.. In the case of the film blends, monomer production is more evident for head-to-head PVC, since the peaks corresponding to hydrogen chloride and monomer production are not co-incident,and hence early monomer production can be easily detected. Whereas, with PVC Breon 113 monomer production is indicated by the appearance of material condensable at ~100°C at the dehydrochlorination peak.



Differential condensation TVA curves for simultaneous degradation of PVC Breon 113 and PMMA powder samples, 20 mg of each.

Effect of Other Variables on Blends of Head-to-head PVC with PMMA

Ratio of Polymers

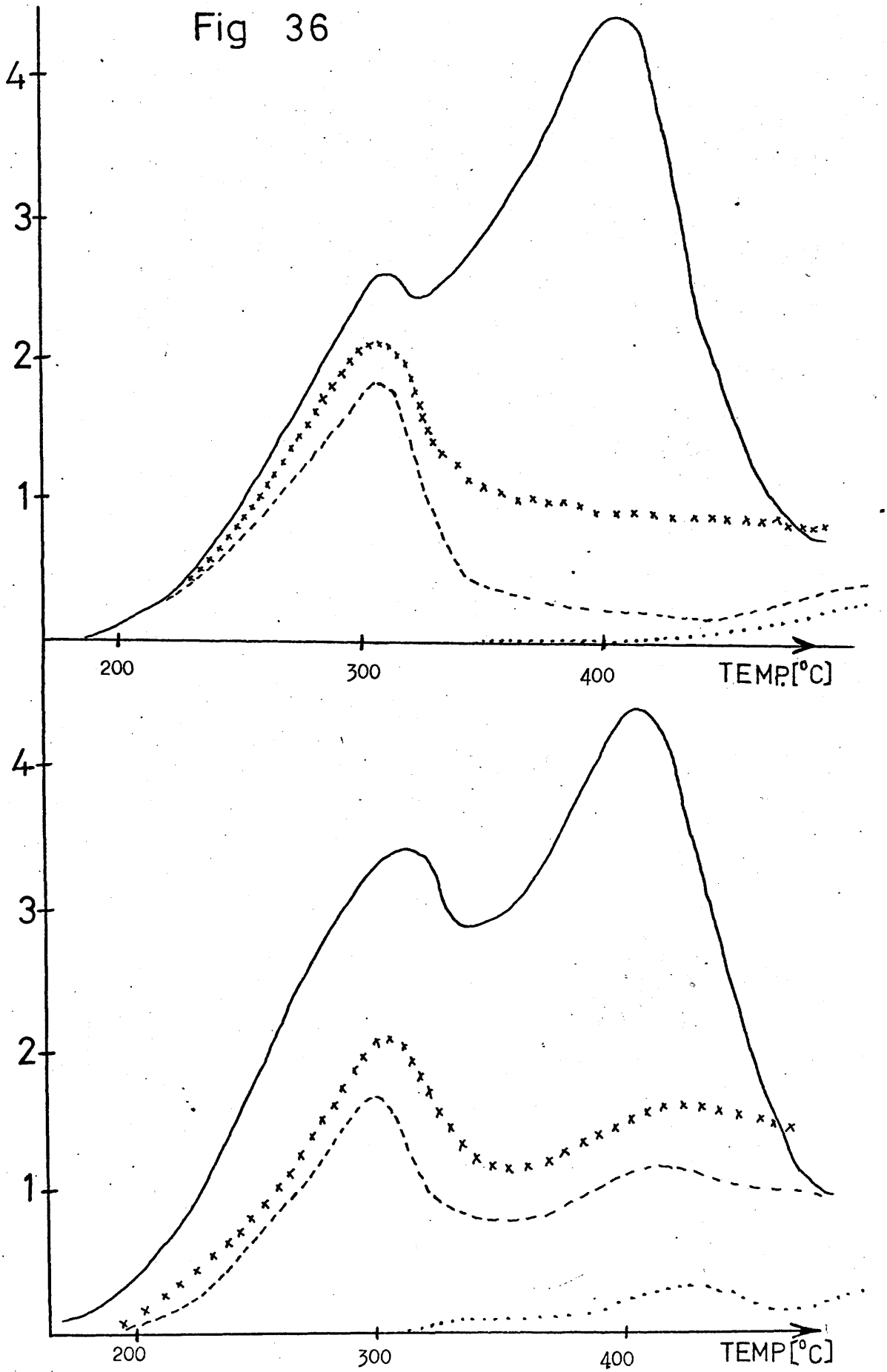
The effects described overleaf were also investigated when the ratio of PMMA to head-to-head PVC was altered. Polymer blends were prepared in which the ratio of the polymers was 10:1, 5:1, 2:1, 1:2, 1:5 and 1:10 respectively. TVA curves were obtained for these blends and for the corresponding unmixed samples. Enhanced depolymerisation was observed in the mixed sample in every case, even when head-to-head PVC formed only 10% of the blend. The curves obtained when the ratio of head-to-head PVC to PMMA was 1:5 are shown in Fig.36.

Thermogravimetric Studies of Powders

(a) PMMA/head-to-head PVC

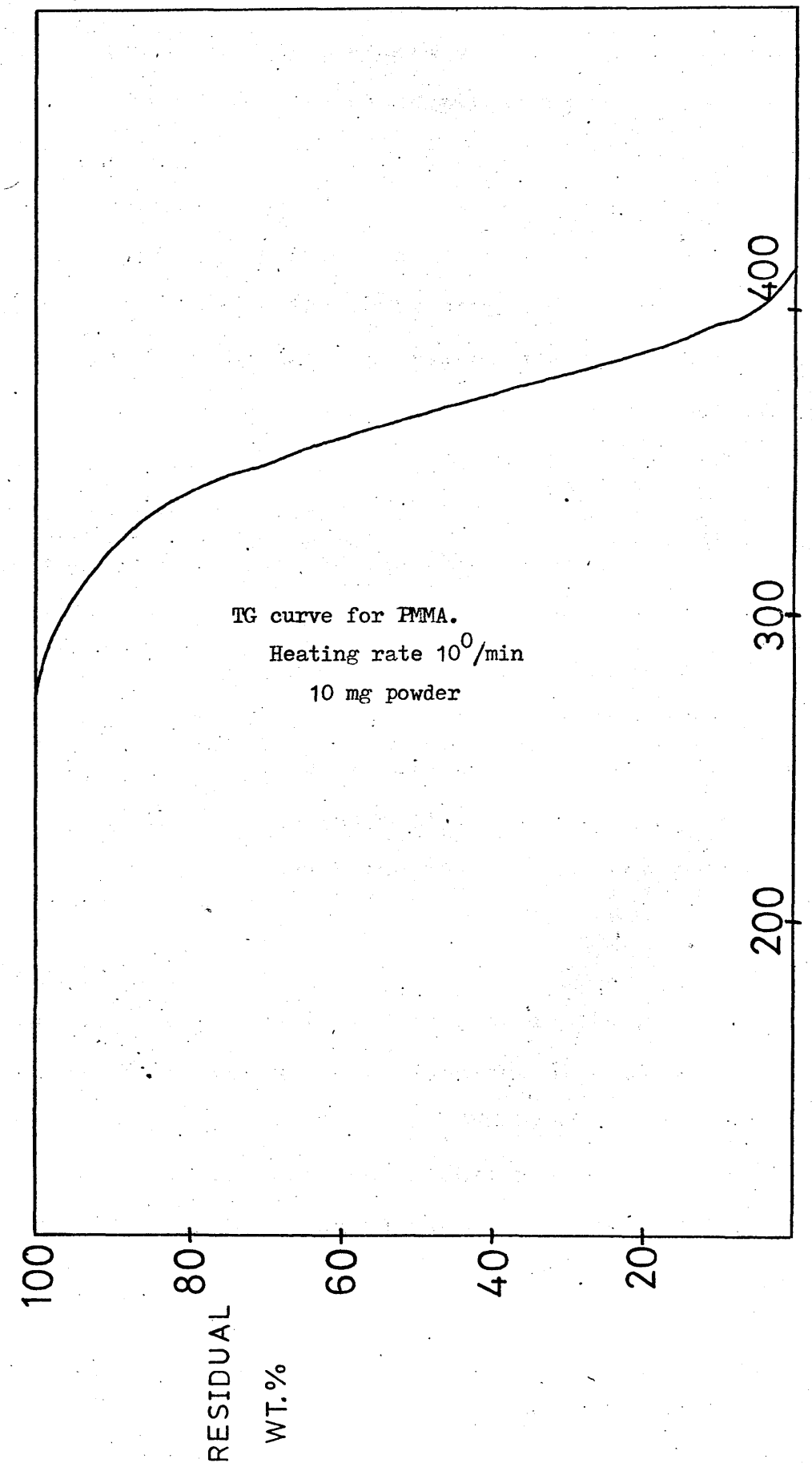
Due to the limitations of the Du Pont thermobalance, no high vacuum degradations could be carried out on powder blend systems. Experiments were carried out under a dynamic nitrogen atmosphere. TG curves for head-to-head PVC and PMMA are shown in Figs. 16 and 37 respectively. The shape of the TG curve for head-to-head PVC has been discussed previously in Chapter 4. The TG curve for PMMA shows a smooth one-stage depolymerisation reaction, with no residual weight loss after 400°C. To obtain a TG curve for an "unmixed" powder sample, the following method was used. The TG curves obtained for head-to-head PVC and PMMA were superimposed on one another as shown in Fig. 38. The resultant of these two

Fig 36



DC-TVA curves for simultaneous degradation of head-to-head PVC 4 mg, and PMMA 20 mg. (a) unmixed (b) mixed. : Film samples

Fig 37


TG curve for PMMA.
Heating rate 10°/min
10 mg powder
RESIDUAL WT.%
100
80
60
40
20
TEMPERATURE [°C]
200
300
400

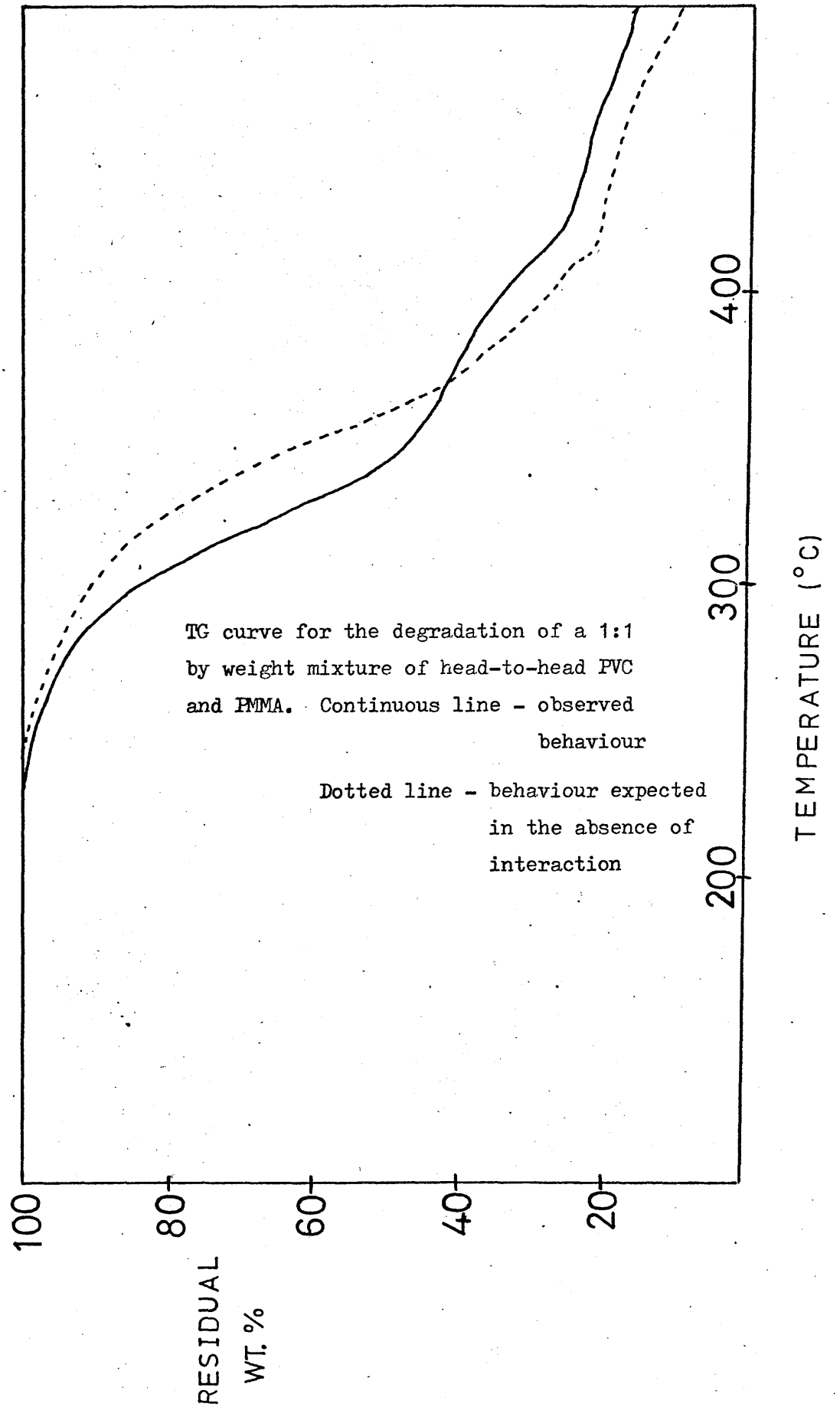
curves was now drawn, and this was taken to represent the behaviour of a 1:1 mixture by weight in the absence of any interaction. This is compared with the actual experimental TG curve obtained for a 1:1 mixed powder blend of the two polymers, which is also shown in Fig. 38. The behaviour of the blend is markedly different from that expected in the absence of interaction. Weight loss is considerably greater in the blend in the early stages of degradation (below 250°C). In the later stages of degradation, however, the weight loss of the blend system is less than that of the unmixed sample.

These results may be interpreted as follows. Interaction between the head-to-head PVC and PMMA results in increased production of methyl methacrylate due to enhancement of the depolymerisation reaction as previously described. However, at higher temperatures, hydrogen chloride attack on the ester groups of PMMA causes stabilisation by formation of anhydride rings. This enhanced stability is also demonstrated by a larger residue in the blend than in the unmixed system.

(b) PMMA/PVC Breon 113

Using the same method as that described in the previous section (a), TG curves were obtained for 1:1 mixed and unmixed powder samples of PMMA and PVC Breon 113. These are shown in Fig. 39. Interaction is observed in the mixed powder sample, but mainly at higher temperatures. Between

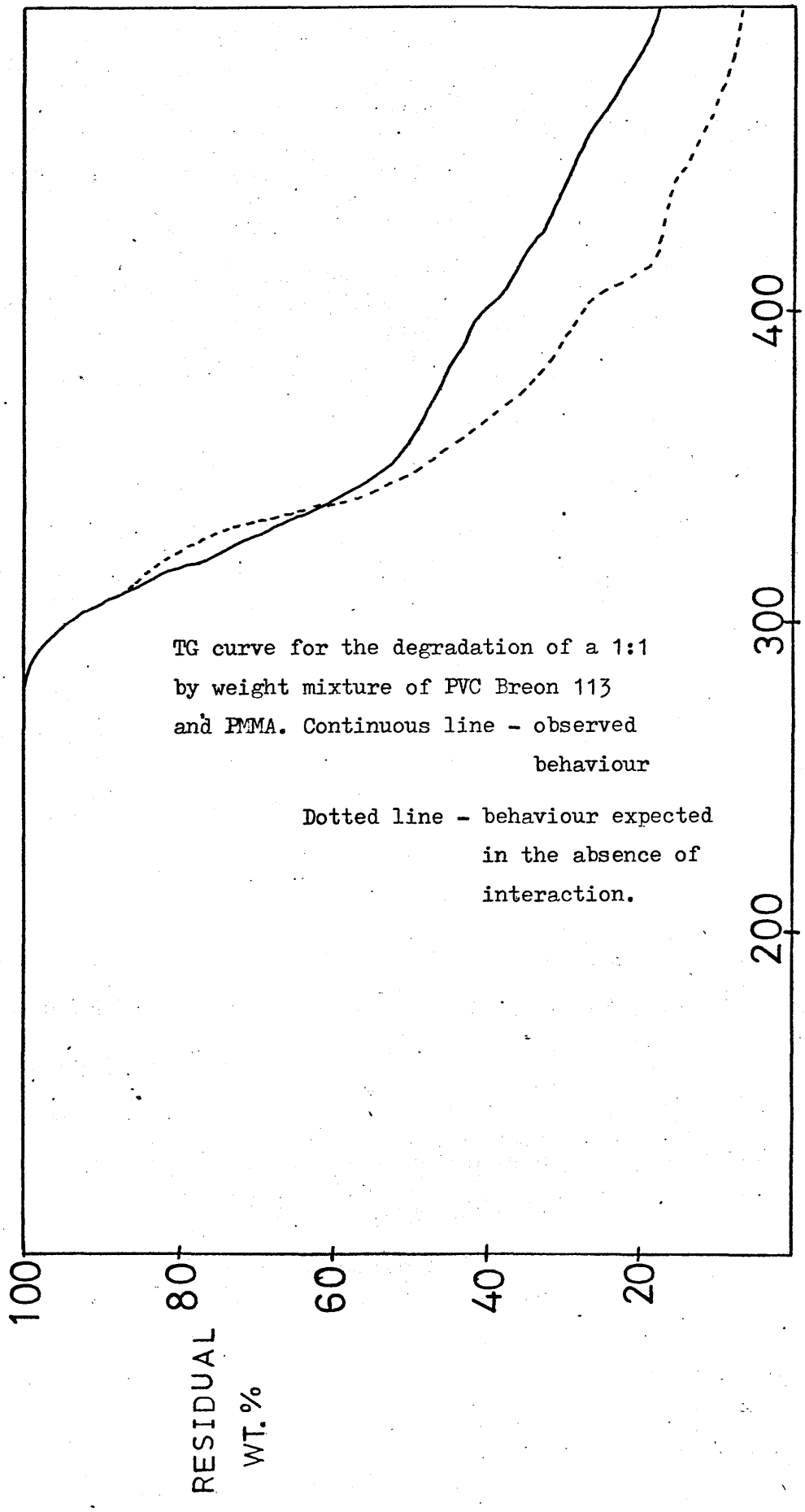
Fig. 38



TG curve for the degradation of a 1:1 by weight mixture of head-to-head PVC and PMMA. Continuous line - observed behaviour

Dotted line - behaviour expected in the absence of interaction

Fig 39



TG curve for the degradation of a 1:1 by weight mixture of PVC Breon 113 and PMMA. Continuous line - observed behaviour

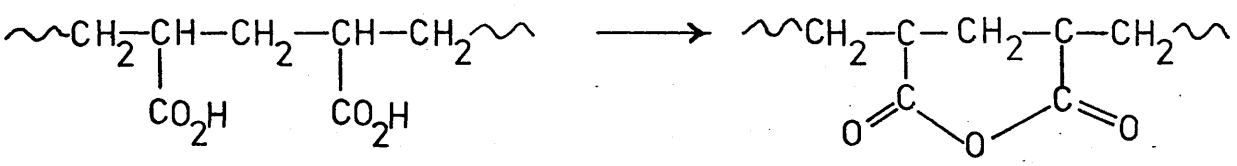
Dotted line - behaviour expected in the absence of interaction.

300° and 350°, weight loss from the mixed sample is slightly greater than from the unmixed sample, however above 350°, the mixed system appears to be more stable, since the weight loss is reduced considerably and an increased residue is observed.

Products of Degradation from Blends of Head-to-head PVC with PMMA

Anhydro-poly(methacrylic acid)

When poly(methacrylic acid) is heated, water is eliminated and six-membered anhydride ring structures are formed[24]. The resulting polymer is known as anhydro-poly(methacrylic acid).



Grant and Grassie[24] have studied this polymer in detail and observed bands at 1795, 1750 and 1022cm^{-1} in the infra red spectrum, characteristic of six-membered anhydride ring structures. The degradation of anhydro-poly(methacrylic acid) has been shown to produce carbon dioxide, carbon monoxide, and methane[37] from the break-up of the six-membered rings, with a peak maximum in the TVA at 450°C.

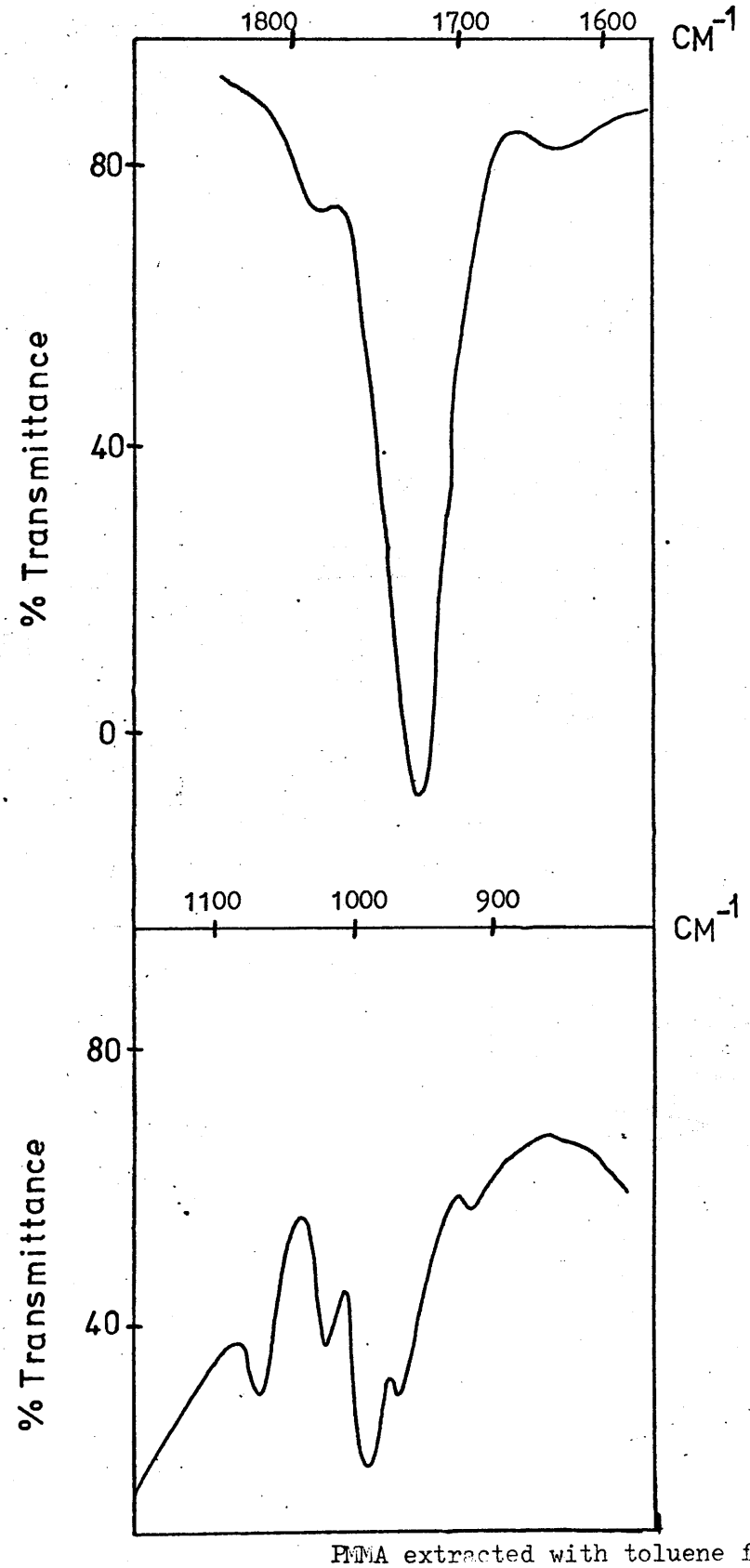
It is thought to be this type of structure which is formed by the effect of hydrogen chloride on PMMA during degradation. McNeill and Neil[37,88] have demonstrated this in their work on PMMA/PVC blends. They extracted PMMA from partially degraded blends and showed that the resulting polymer displayed peaks at 1800 and 1020 cm^{-1} in the infra red spectrum, corresponding to six-membered anhydride ring structures. An alternative method used was to cast a mixed film directly on to a sodium chloride disc. The disc was placed in a degradation tube and at various temperatures the disc was removed and placed directly into an infra red spectrometer. The infra red spectra for pure PMMA and PMMA extracted from a partially degraded mixed film blend with head-to-head PVC are shown in Fig. 40. Bands are clearly visible at 1795 and 1020cm^{-1} in the mixed blend, providing strong indication that anhydride rings may be present in PMMA degraded in the presence of head-to-head PVC.

Volatile products of degradation

(a) Head-to-head PVC/PMMA blends

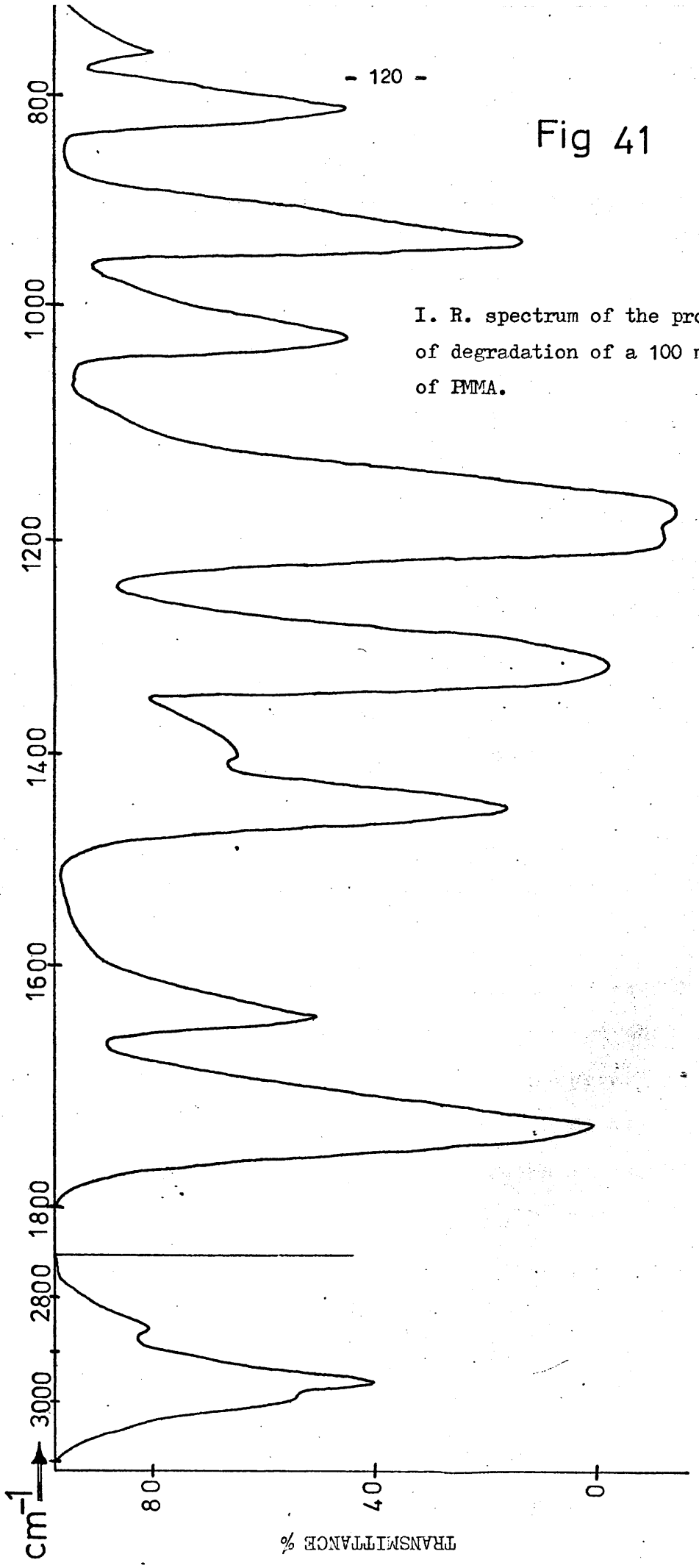
100 mg. samples of PMMA and head-to-head PVC were degraded separately as films in the TVA apparatus. The samples were first pre-heated to 80°C under vacuum in order to remove all traces of solvent. After degradation was completed (500°C) the products were collected, as described in Chapter 2, and infra red spectra were obtained. The spectrum of PMMA in Fig. 41 shows only methyl methacrylate, while the products

Fig 40



PMMA extracted with toluene from a PMMA/head-to-head PVC film heated to 325° at 10°/min

Fig 41



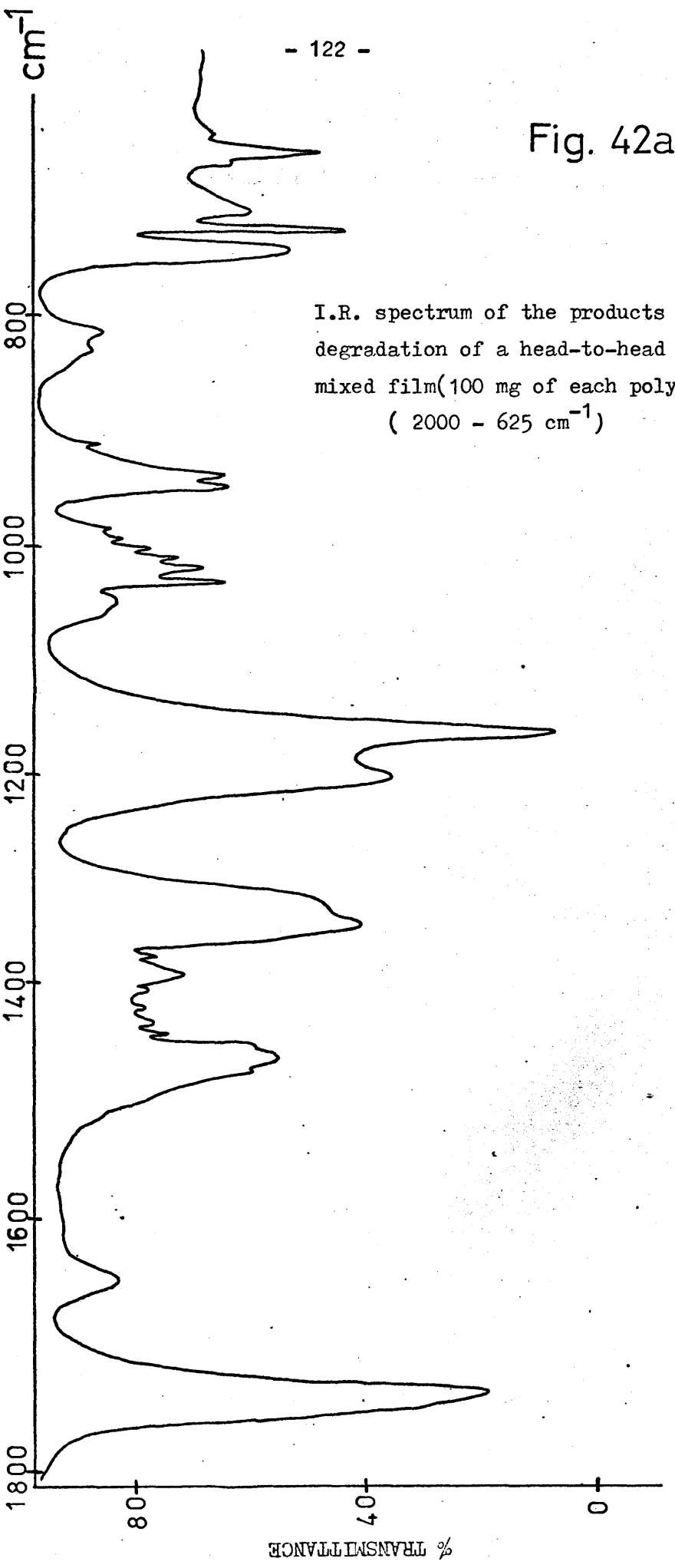
I. R. spectrum of the products of degradation of a 100 mg. film of PMMA.

of degradation of head-to-head PVC have been discussed previously in Chapter 4. Only hydrogen chloride appears as a major degradation product, while trace amounts of ethylene and propylene are also present. A 1:1 mixed film blend of PMMA and head-to-head PVC was heated to 500°C at 10°/min. and the products collected in the range 150° to 450°, this being chosen to exclude solvent evolved at low temperatures and other products from the later stages of degradation of head-to-head PVC. The spectrum of the products from the degradation of the blend is shown in Fig. 42. The bands at 2320, 3700 and 670 cm^{-1}, indicate carbon dioxide, while there is no evidence for the presence of carbon monoxide. By analogy with anhydro-poly(methacrylic acid), methane is predicted as a product, but its strongest absorption band at 3020 cm^{-1} is totally obscured by hydrogen chloride absorption. Hence there is no evidence in the spectrum for methane production.

Two other important products, however, can be easily detected from the blend. These are methanol and methyl chloride. Methyl chloride can be detected by its characteristic three-band absorption between 700 and 750 cm^{-1}. It also gives fine structure at 1350 to 1450 cm^{-1}, which is plainly visible, while the other fine absorption pattern at 1000 to 1100cm^{-1} is partially obscured by another absorption not present in the unmixed system.

Methanol has also a distinct three-band absorption pattern which occurs at 1020, 1030 and 1050 cm^{-1} respectively, while a small O-H vibration can be observed at 3600 cm^{-1}. Apart

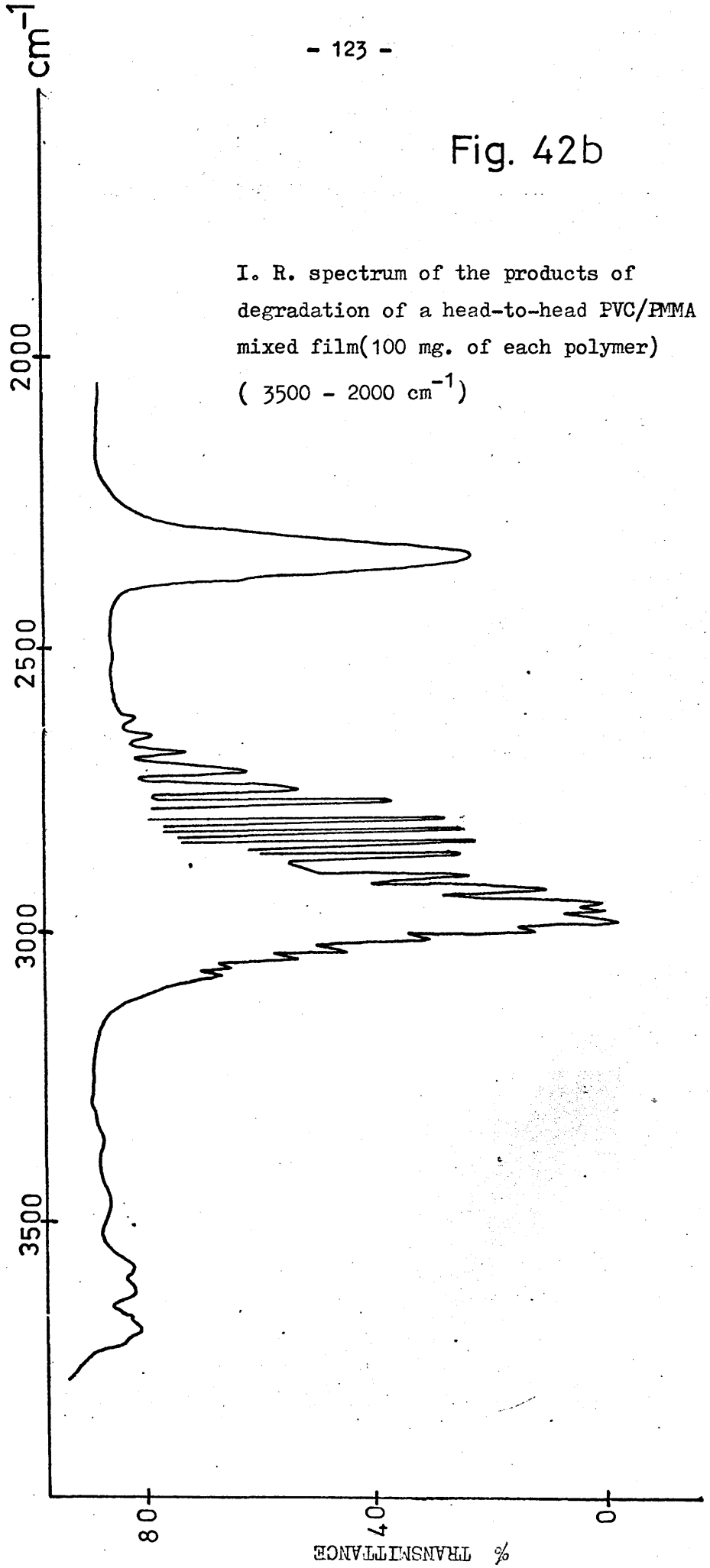
Fig. 42a.



I.R. spectrum of the products of degradation of a head-to-head PVC/PMMA mixed film(100 mg of each polymer)
(2000 - 625 cm^{-1})

Fig. 42b

I. R. spectrum of the products of degradation of a head-to-head PVC/PMMA mixed film(100 mg. of each polymer)
(3500 - 2000 cm^{-1})



from carbon dioxide, methyl chloride and methanol, no other products were observed which were not present in the unmixed system.

(b) PVC Breon 113/PMMA Blends

Infra red spectra were also obtained for the products of degradation of mixed and unmixed 1:1 blends of PVC Breon 113 with PMMA. In the spectrum of the products for the mixed system, the only new product identifiable was carbon dioxide. Neither methanol nor methyl chloride could be detected from the infra red spectrum. McNeill and Neil[37,88] obtained a similar spectrum for the PVC/PMMA system although they subsequently detected methyl chloride by mass spectrometric analysis.

Effect of Hydrogen Chloride on PMMA

McNeill and Neil[37,88] proposed a mechanism for the formation of anhydrides in PMMA by the action of hydrogen chloride. This mechanism required both methanol and methyl chloride to be produced in equimolar amounts, and was thus open to doubt since methanol could not be detected. Although both of these products can be readily detected by infra red spectroscopy in blends of head-to-head PVC with PMMA, it was impossible to determine their relative amounts directly. Even without this further piece of evidence, it appears that the mechanism proposed by these authors holds in the case of hydrogen chloride production in head-to-head PVC.

Estimation of Methyl Methacrylate by Gas-liquid Chromatography

From a previous discussion of blends of head-to-head PVC with PMMA, it can be seen that in the blend an increased amount of methyl methacrylate is produced in the early stages of degradation. In order to quantify this effect gas-liquid chromatographic (GLC) analysis was carried out on the methyl methacrylate produced from PMMA alone and from mixed blends of PMMA with head-to-head PVC.

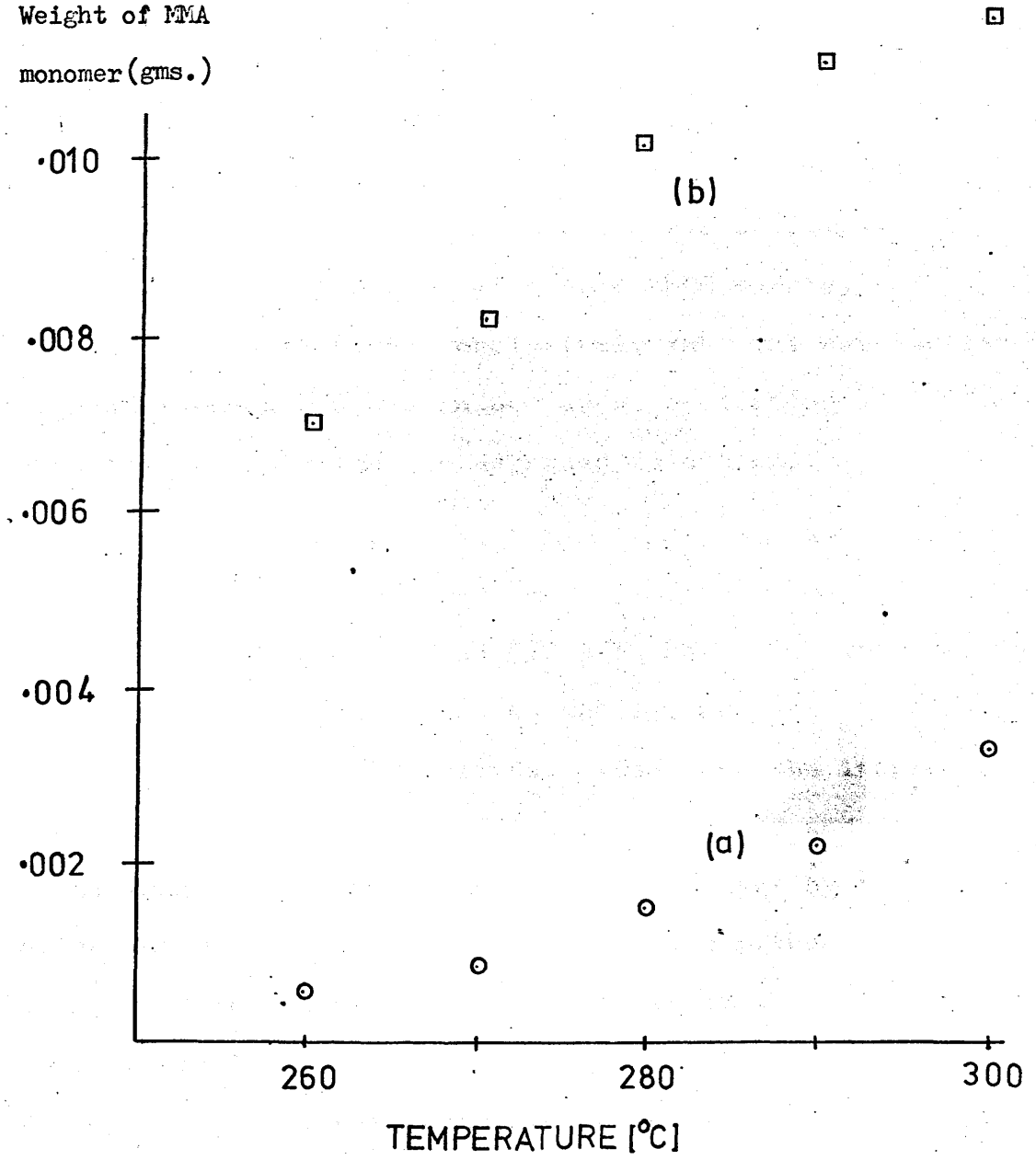
A 100 mg. film sample of PMMA was degraded in the TVA apparatus, the degradation stopped at 250°C and the products analysed by GLC. Separations were carried out on a 1 per cent SE 30 column, with helium as carrier gas and using a flame ionization detector. The chromatographic column was programmed at 10°/min., the program being started immediately after sample injection.

Quantitative results were obtained by using the method described in Chapter 2. This process was repeated for further 100 mg. samples of PMMA under conditions where the degradation was stopped at 260, 270, 280, 290, and 300°C. respectively, and the products were collected and analysed as before.

A 1:1 polymer blend of PMMA and head-to-head PVC was prepared, containing 100 mgs. of each. Degradation was carried out as before and again stoped at 250°C. The products were collected and analysed for methyl methacrylate. Further 1:1 mixed blend samples were degraded under conditions where the degradation was stopped at 260, 270, 280, 290 and 300°C respectively and the products analysed for methyl methacrylate.

Fig 43

Cumulative yield of methyl methacrylate from (a) 100 mg film of PMMA
(b) 100 mg of PMMA in a mixed film blend with 100 mg of head-to-head PVC.
Both (a) and (b) heated at 10°/min.



The results for methyl methacrylate production from the pure polymer and the blend for temperature-programmed degradation are compared in Fig. 43. A large increase in methyl methacrylate production is observed in the case of the polymer blend.

Similar results were obtained under isothermal degradation conditions (250°C). When the polymers were degraded simultaneously as "unmixed" films using the special trouser-tube, methyl methacrylate production was identical to that observed from degradation of a pure PMMA sample.

Hence the results prove conclusively that the degradation of head-to-head PVC can induce depolymerisation of PMMA, when the two polymers are degraded in a blend.

CONCLUSION

Film blends of head-to-head PVC with PMMA show the two types of interaction as discussed by McNeill and Neil[37,88] in their study of PMMA/PVC blends. These are the increased depolymerisation of PMMA at low temperatures and the stabilisation of PMMA at higher temperatures by the formation of anhydride ring structures. Since the authors have attributed the former of these effects to the presence of small radicals from the degrading PVC, it follows that the degradation of head-to-head PVC is accompanied by the presence of radical species.

Although the behaviour of blends of PMMA with head-to-head and head-to-tail PVC are closely similar, it is worthwhile to have a look at some of the observed differences.

Firstly, TG studies show that the difference between calculated and observed weight loss is greater for the PMMA/head-to-head PVC blend system. Secondly, the production of methanol, methyl chloride and carbon dioxide from the attack of hydrogen chloride on the PMMA chains is greatly enhanced in the case of PMMA/head-to-head PVC blends. It is clear from the above observations that the degree of interaction is greater in PMMA/head-to-head PVC blends although it is difficult to explain the differences in terms of chemical interaction since hydrogen chloride is the major product from both types of PVC.

McNeill and Neil[37,88] have explained the interaction in PMMA blends in terms of the diffusion of radical species. Hence the greater degree of interaction observed in blends with head-to-head PVC might be expected to be reflected in the melting point values.

However this is not the case since head-to-head PVC retains its sample form at 500°C, while melting point values of head-to-tail PVC are considerably lower[98,99]. It is also worthwhile noting that the T_g value for head-to-head PVC[100] is almost the same as for conventional head-to-tail PVC.

POLYMER BLENDS

(A) Blends of head-to-head PVC with polystyrene and poly (methacrylic acid).

The thermal degradation of these systems was studied, and the results obtained are summarised in Table 11. Due to lack of time, the study of these systems was restricted to differential condensation TVA of the mixed and unmixed samples using the special trouser-tube described previously.

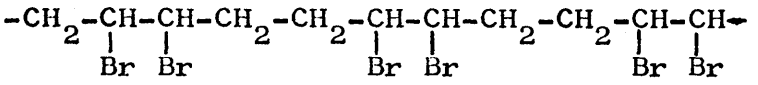
TABLE 11

Polymer pair	TVA behaviour of mixed sample compared to unmixed
1. Head-to-head PVC and polystyrene	Styrene production occurs at higher temperature (about 30°C higher). No change in peak associated with the dehydrochlorination of head-to-head PVC.
2. Head-to-head PVC and poly(methacrylic acid)	Degradation of anhydro-poly (methacrylic acid) occurs at higher temperature (about 20°C higher). 20°C. stabilisation in peak associated with dehydrochlorination of head-to-head PVC
3. Head-to-tail PVC[101] and polystyrene.	Styrene production occurs at higher temperature (about 20°C higher). Peak associated with dehydrochlorination shows a 20°C stabilisation.
4. Head-to-tail PVC and poly(methacrylic acid)[102]	No change in peak associated with the dehydrochlorination of head-to-tail PVC. 30°C. stabilisation in peak associated with degradation of anhydro-poly(methacrylic acid)

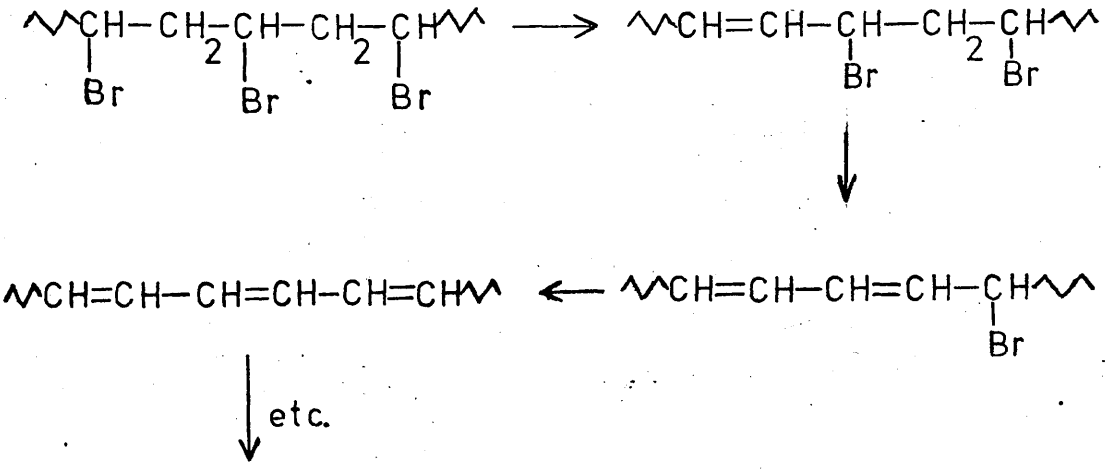
CHAPTER 6

Head-to-Head Poly(vinyl bromide)

Head-to-head poly(vinyl bromide) is the bromine analogue of the polymer studied extensively in Chapter 4 and has the structure shown



The polymer has been prepared previously,[6, 11] although no attempt has been made to study its thermal properties. The corresponding head-to-tail PVBr has been studied and the degradation process fairly well characterised[102] Breakdown occurs by elimination of hydrogen bromide, and by the build-up of polyene sequences, which have been shown to be longer than those found in the degradation of head-to-tail PVC[53]. The following mechanism has been postulated for the dehydrobromination reaction occurring during the degradation of head-to-tail PVBr.



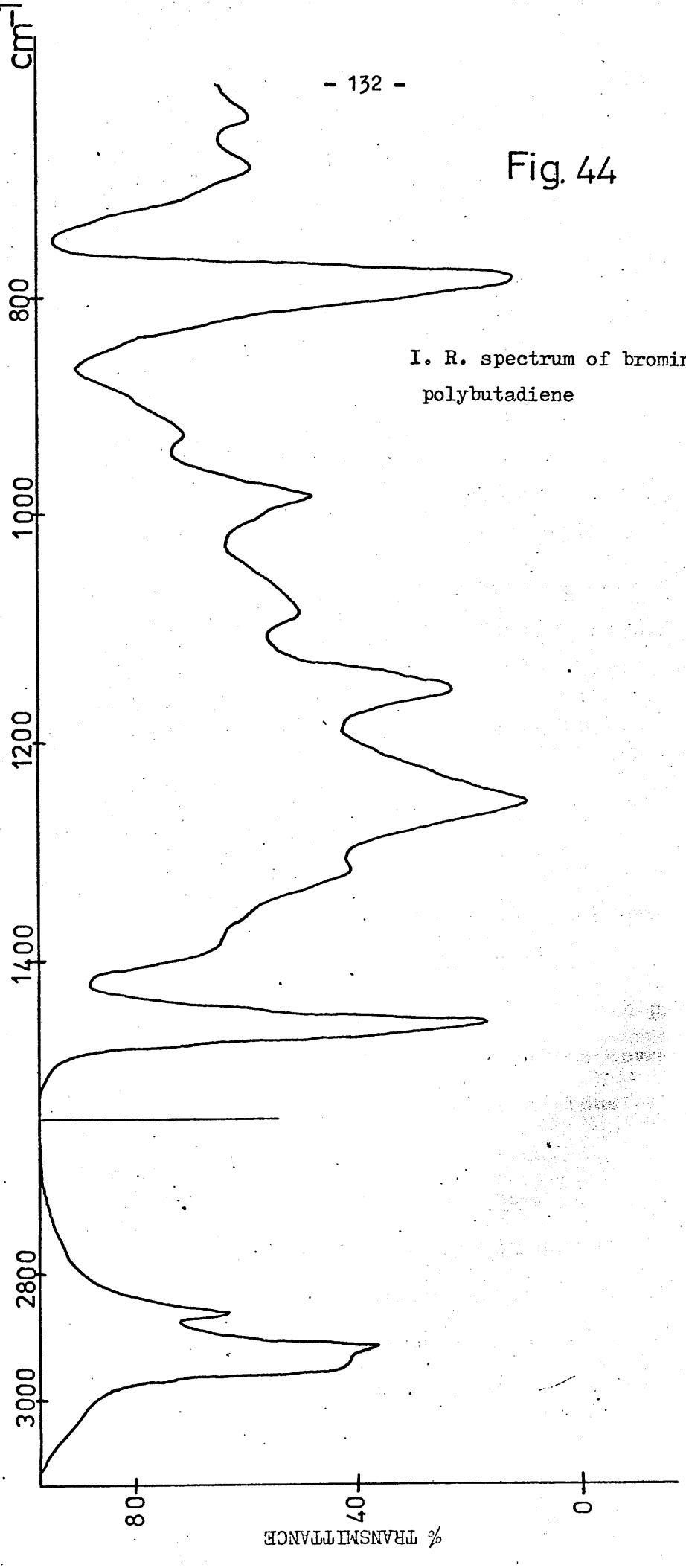
An explanation has been offered for the formation of these longer sequences. After the first few eliminations in a sequence, the additional energy gained by the system by further extension of the conjugation, begins to diminish, so that a point is reached where the thermodynamic driving force is insufficient to justify elimination of another molecule. Since the C-Br is weaker than the C-Cl bond, it follows that longer polyene sequences will be built up in PVBr before the system has insufficient energy for a further elimination.

A study of head-to-head PVBr was undertaken using the same thermal techniques as before, in order that its behaviour could be related to that of head-to-head PVC and to provide by means of this comparison further insight into the mechanism of degradation of head-to-head PVC.

Preparation of Head-to-head PVBr

The preparation of head-to-head PVBr was achieved by bromination of polybutadiene. The method used was similar to that decribed in Chapter 3 for the chlorination of polybutadiene. Molecular bromine was added to solutions of polybutadiene in methylene chloride. The reaction ceased when the bromine content reached approximately 73.5% by weight. An infra red spectrum of the brominated polymer is shown in Fig. 44. The spectrum is similar to that of the chlorinated polymer, the only difference being in the absorptions below 750cm^{-1}. In Fig. 44, the band at 625 cm^{-1} is due to stretching of

Fig. 44



I. R. spectrum of brominated polybutadiene

the C-Br bond.

Thermal degradation of head-to-head PVBr

The TVA curve at a heating rate of 10°/min. for purified head-to-head PVBr is shown in Fig. 45. The curve consists of a major peak having a T_{max} at 250°C. and a minor at 490°C. As will be shown later by product analysis, the material evolved in the early stages of degradation which is condensed at -196°C corresponds to hydrogen bromide. Breakdown commences at 115°C., while the elimination appears to be a smooth one-stage process, and is completed long before secondary breakdown of the polymer backbone occurs.

Thermogravimetry (TG)

The above pattern is confirmed if the TG curve for the polymer is examined. Fig 46 shows that breakdown commences at 115°C with smooth weight loss to 300°C., when the polymer has lost approximately 74% by weight. A smooth plateau region continues until secondary degradation commences around 400°C., leaving a 20% by weight residue at 500°C.

Analysis of the products of degradation

A 50mg. sample of head-to-head PVBr was degraded using the TVA apparatus and the degradation was stopped after the first peak. The products were collected and an infra red spectrum was obtained. The spectrum showed only the presence of hydrogen bromide, characterised by a multiple absorption

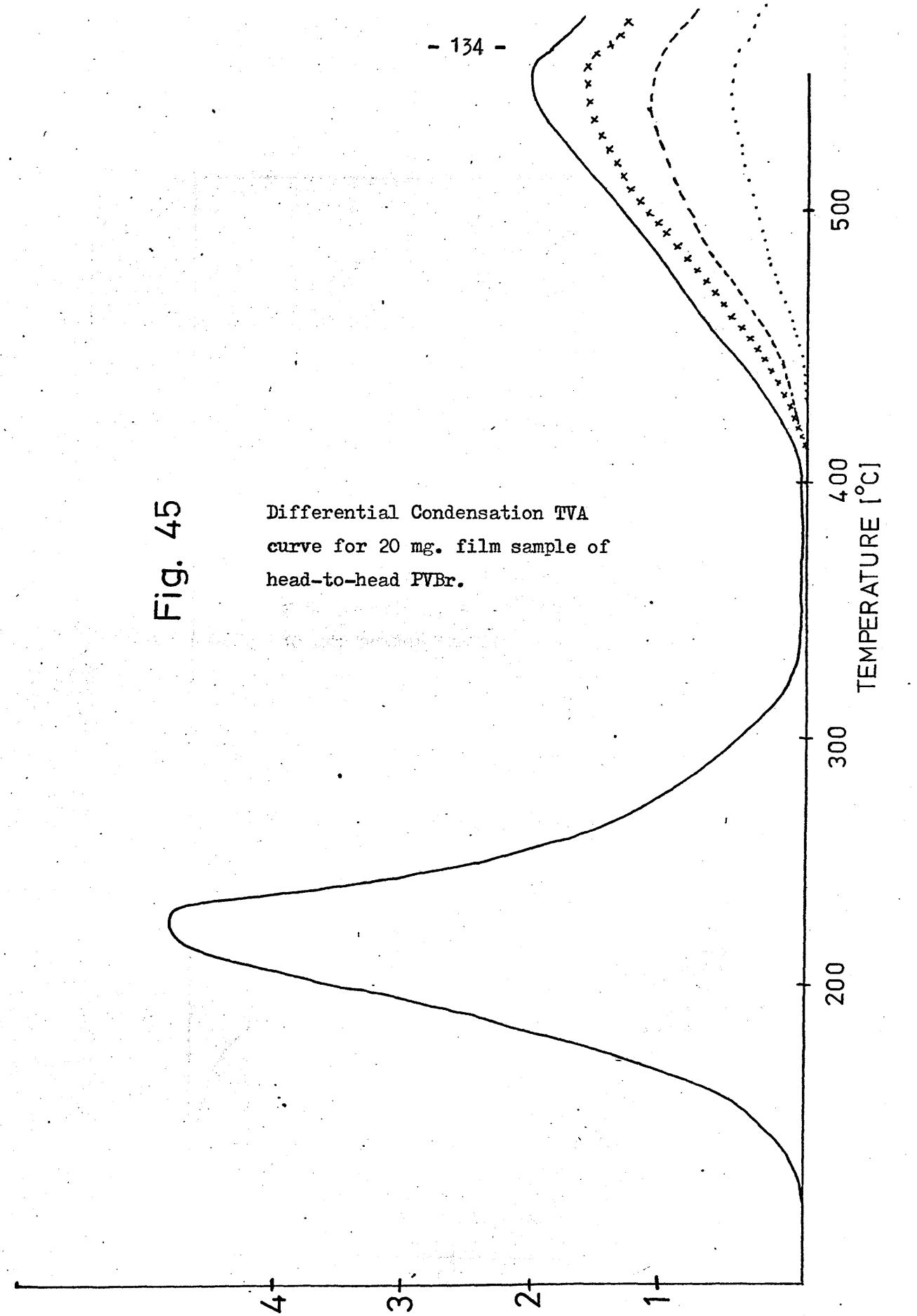
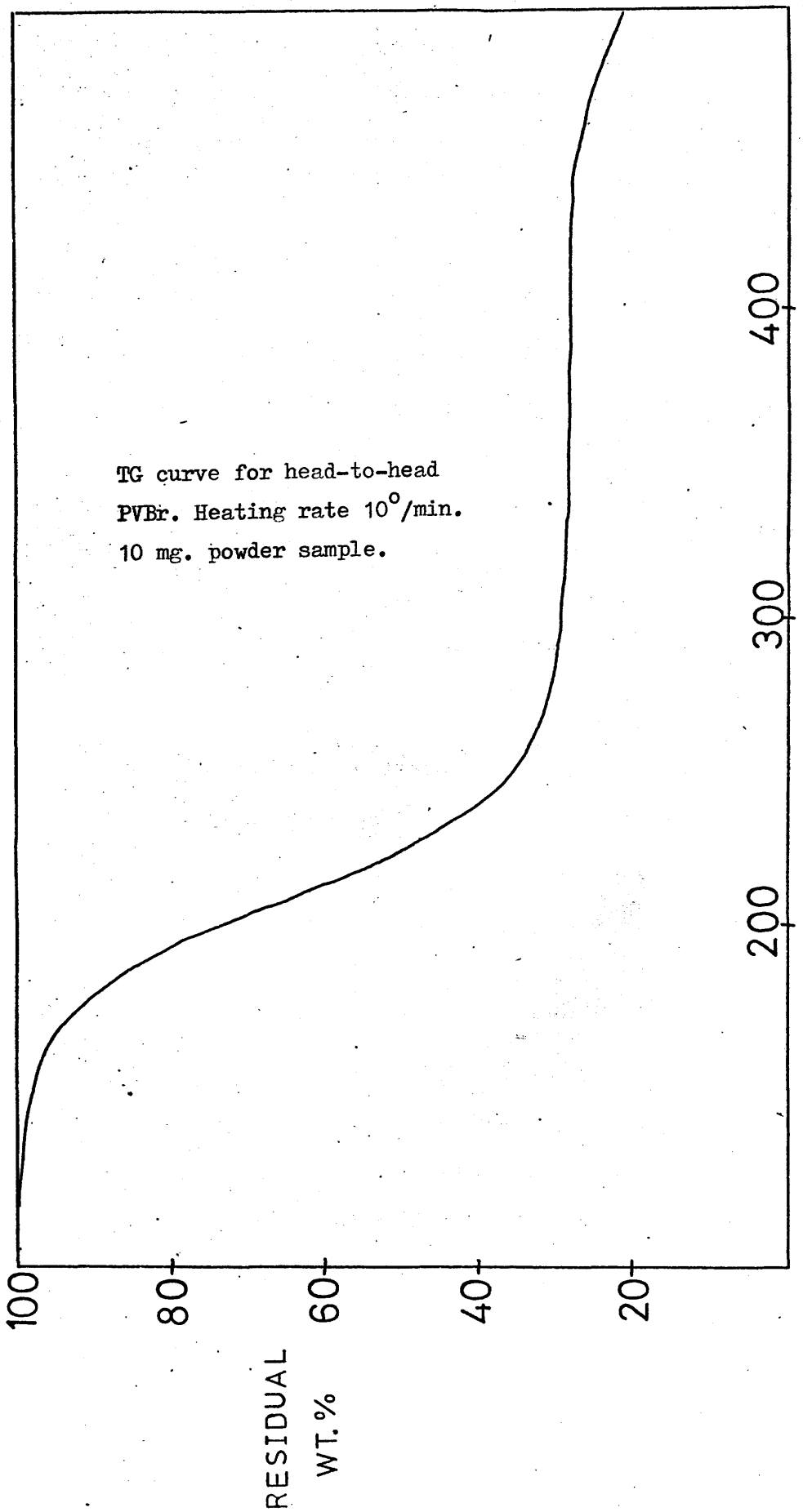


Fig. 45

Differential Condensation TVA curve for 20 mg. film sample of head-to-head PVBr.

Fig 46


TG curve for head-to-head
PVBr. Heating rate 10°/min.
10 mg. powder sample.
100
80
60
40
20
RESIDUAL
WT.%
200
300
400
TEMPERATURE [°C]

centred on 2560 cm^{-1}. In a second, similar experiment the products corresponding to the secondary peak in the degradation were collected. The infra red spectrum showed only traces of ethylene and propylene.

(b) Cold-ring fraction

The cold-ring fraction did not appear until secondary degradation of the polymer chain had started around 400°C. An infra red spectrum showed that the cold ring fraction was identical to that obtained for head-to-head PVC, containing small, unsaturated, hydrocarbon units.

(c) Residue

The residue at the end of degradation was a black powder. Melting had not occurred since the sample form was unchanged. Infra red analysis revealed an unsaturated hydrocarbon, similar to that obtained from degradation of head-to-head PVC.

Ultra Violet Spectroscopy

A series of spectra similar to that produced in Chapter 4 for head-to-head PVC could not be obtained since the special silica degradation tube described in Chapter 2 was unavailable. The films, however, were generally reddish in colour in the early stages of degradation. Hence it seems most likely that long conjugated sequences are present early in the degradation.

Kinetics of dehydrobromination

Kinetic parameters of the reaction were found using the method of Coats and Redfern[83] discussed previously. The method was applied to a programmed TG curve. The functions $\log (Q/T2)$ where $Q = \frac{1-F^{(1-n)}}{1-n}$ (See Chapter 4) for n = 1 and n = 3/2 were calculated at temperatures 150, 175, 200, 225 and 250°C respectively, and the graphs obtained are shown in Fig. 47.

Since the dehydrobromination reaction goes to completion before secondary breakdown, the method can be applied without error arising from overlap of the two reactions From the graphs, it is evident that there is too much scatter to say which value of n produces less curvature, and so the equations of the best fitting straight lines were calculated for both sets of points. The gradients of the lines were used to determine the activation energy which was found to be

E = 19 Kcals / mole if n = 1

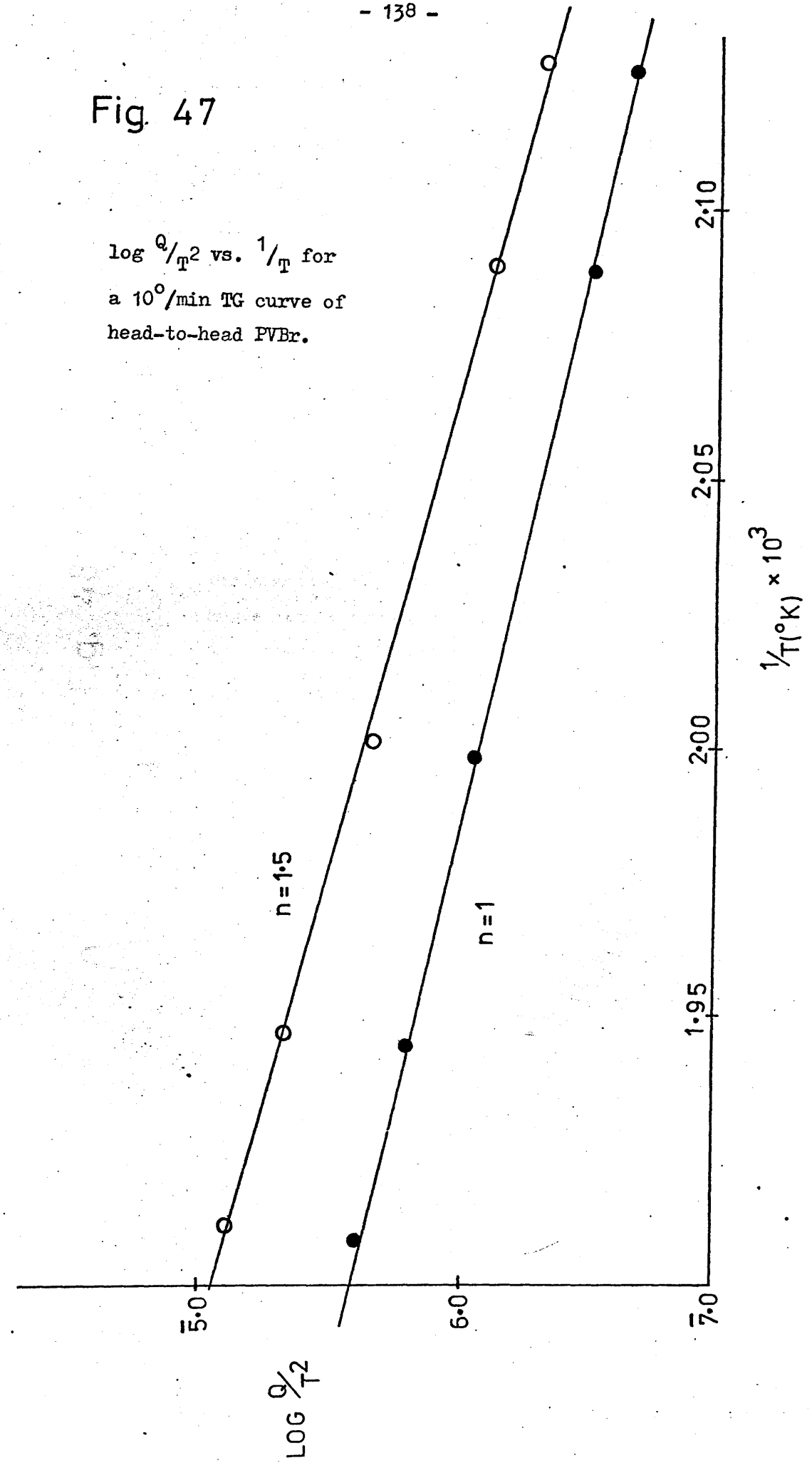
E = 21 Kcals / mole if n = 1.5

Although it is impossible to assign a specific order, the energy of activation is clearly in the region of 20 Kcals/ mole. This value is consistent with a radical reaction.

It is worthwhile at this point to have a brief look at the behaviour of head-to-tail PVBr during degradation. The TVA curve obtained at 10°/min is shown in Fig. 48 . The curve obtained is very similar to that for the head-to-head polymer. The only difference is that breakdown starts at slightly higher temperatures in the case of the head-to-tail polymer,

Fig. 47

log Q/T^2 vs. $1/T$ for a 10°/min TG curve of head-to-head PVBr.



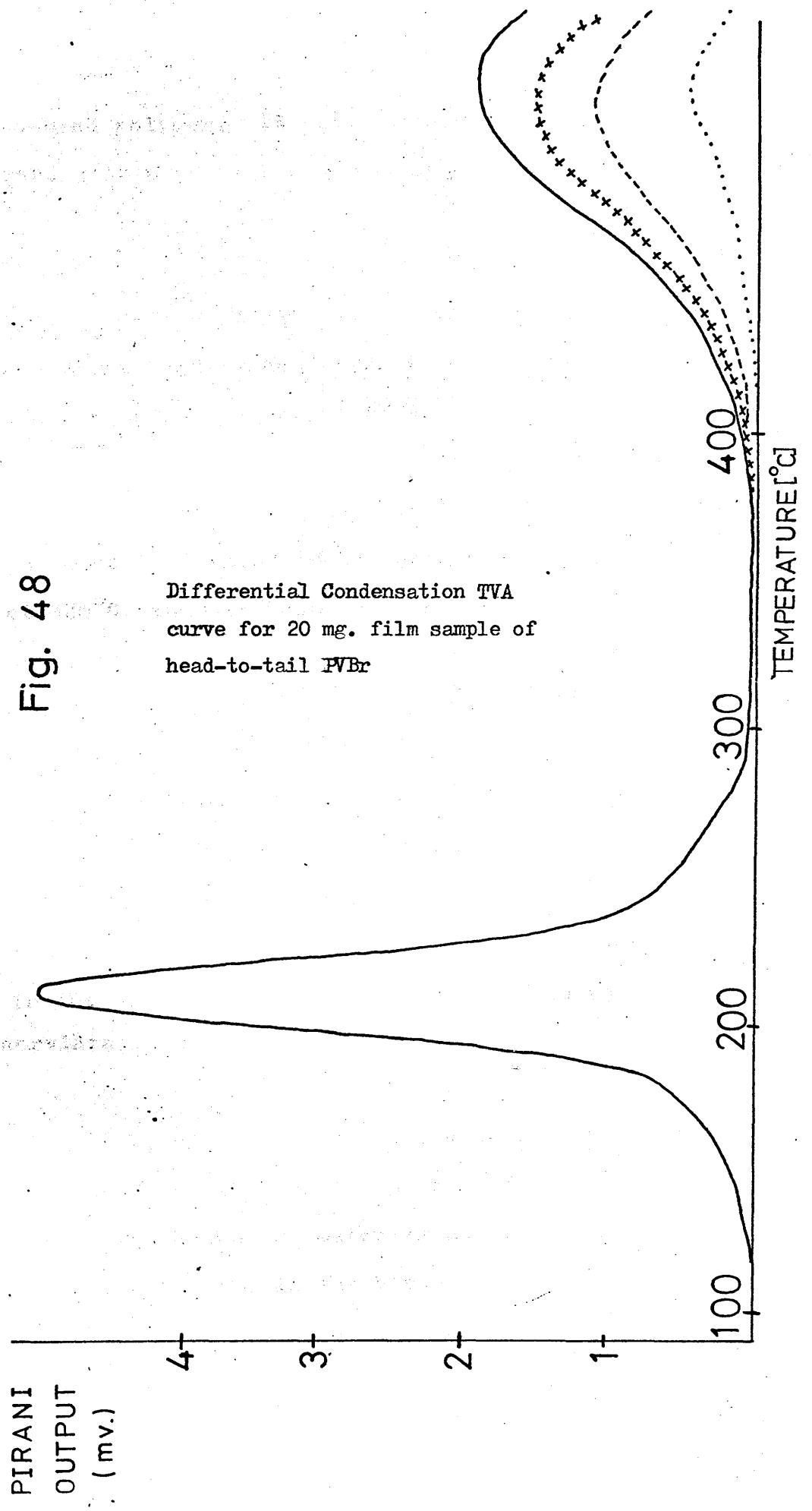


Fig. 48

Differential Condensation TVA curve for 20 mg. film sample of head-to-tail PVBr

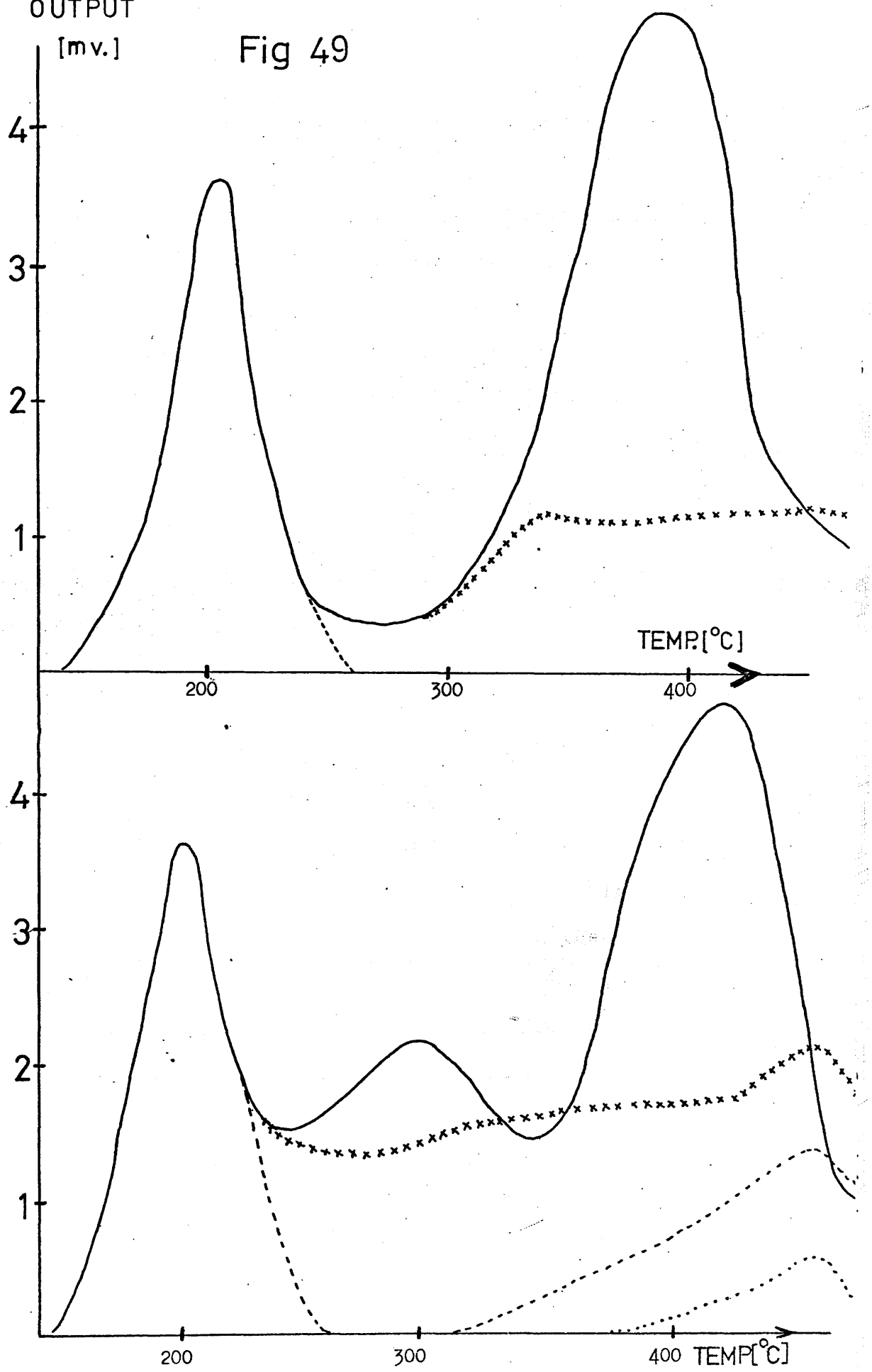
although the T_{max} value is slightly lower than that of the head-to-head polymer. It will be remembered that this was the trend displayed by head-to-head and head-to-tail PVC.

Blends of head-to-head PVBr with PMMA

Film blends of head-to-head PVBr were prepared using both high and low molecular weight PMMA. The TVA curves for mixed and unmixed films of head-to-head PVBr with high molecular weight PMMA are shown in Fig. 49. The TVA curve of high molecular weight PMMA consists of one peak with a T_{max} at 380°C. and has been described in Chapter 5. The TVA curve for unmixed films shows two peaks, the first due to the dehydrobromination reaction of head-to-head PVBr, and the second corresponding to depolymerisation of PMMA. The TVA curve of the mixed film, however, shows three distinct peaks. The peak due to the dehydrobromination remains unaltered, while the new peak at 285°C indicates the presence of material which is condensed at -100° and shows a limiting rate in the -75° trace and hence corresponds to methyl methacrylate monomer.

The third peak, corresponding to the depolymerisation of PMMA, is moved to 410°, while there is a significant increase in the amount of material non-condensable at -196°. Hence the interactions in the blend, are similar to those observed with blends of both head-to-head and head-to-tail PVC with PMMA.

Fig 49



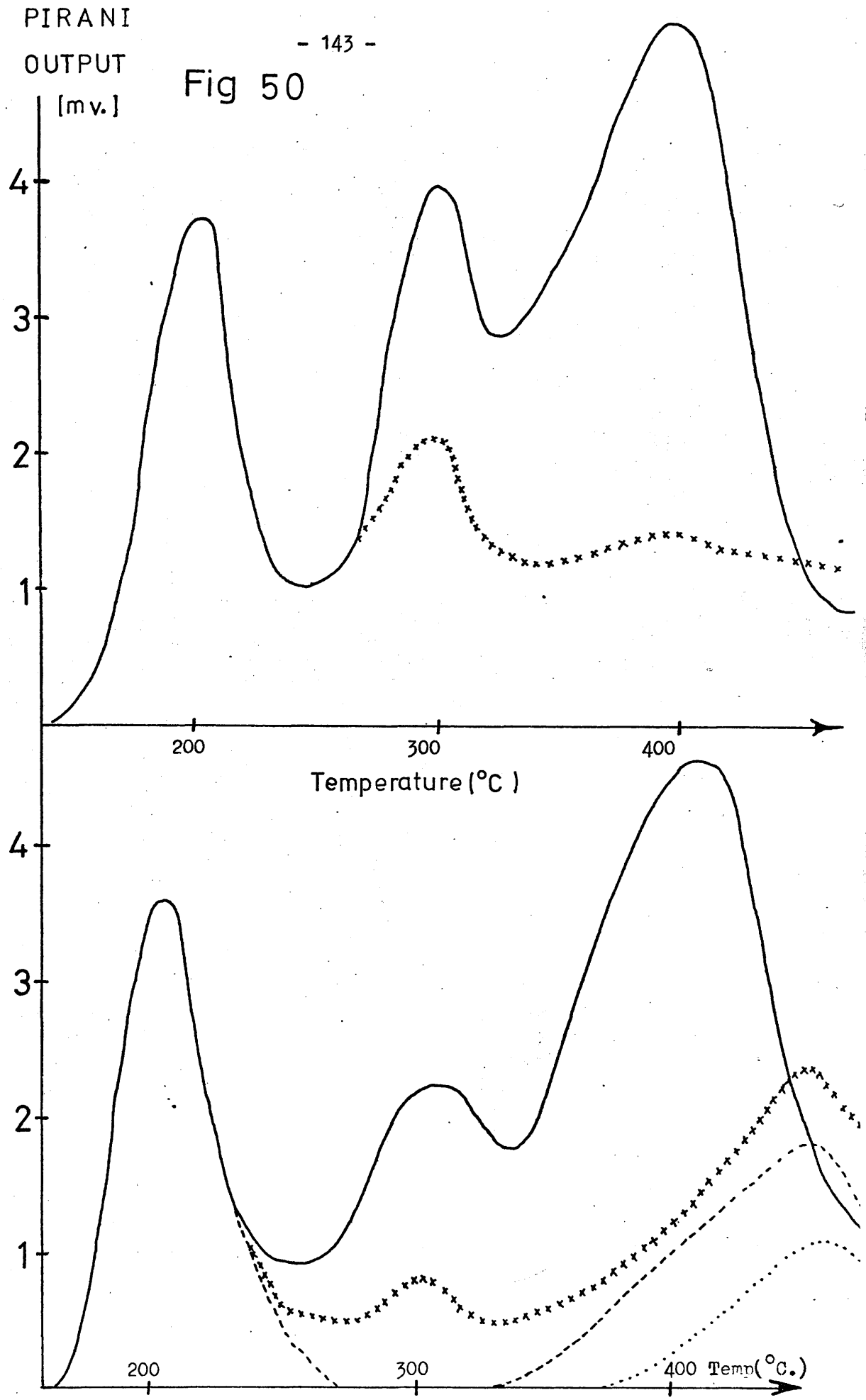
DC-TVA curves for simultaneous degradation of head-to-head PVBr and PMMA(high M.W.),20 mg. of each, (a)unmixed, (b)mixed,: Film samples.

Blends of head-to-tail PVBr with low molecular weight PMMA have been studied previously[102] . The TVA curve of the low molecular weight PMMA shows two peaks, the first at low temperatures due to chain-end initiation, and the second due to random scission. It was observed that in these blends, the chain-end scission process was greatly curtailed, while the peak associated with random scission was moved to higher temperatures with a corresponding increase in the amount of non-condensable material.

Head-to-head PVBr and low molecular weight PMMA were degraded as unmixed and mixed film samples and the TVA curves are shown in Fig. 50. The peak corresponding to the dehydrobromination reaction remains unchanged, however, the two peaks associated with the depolymerisation of PMMA are affected. The peak at lower temperature is considerably reduced in height indicating a curtailment of the chain-end initiation process although no change in the position of the T_{max} is observed. The other peak corresponding to the random chain-scission process is moved 25^{o} to higher temperatures with a significant increase in the amount of non-condensable material.

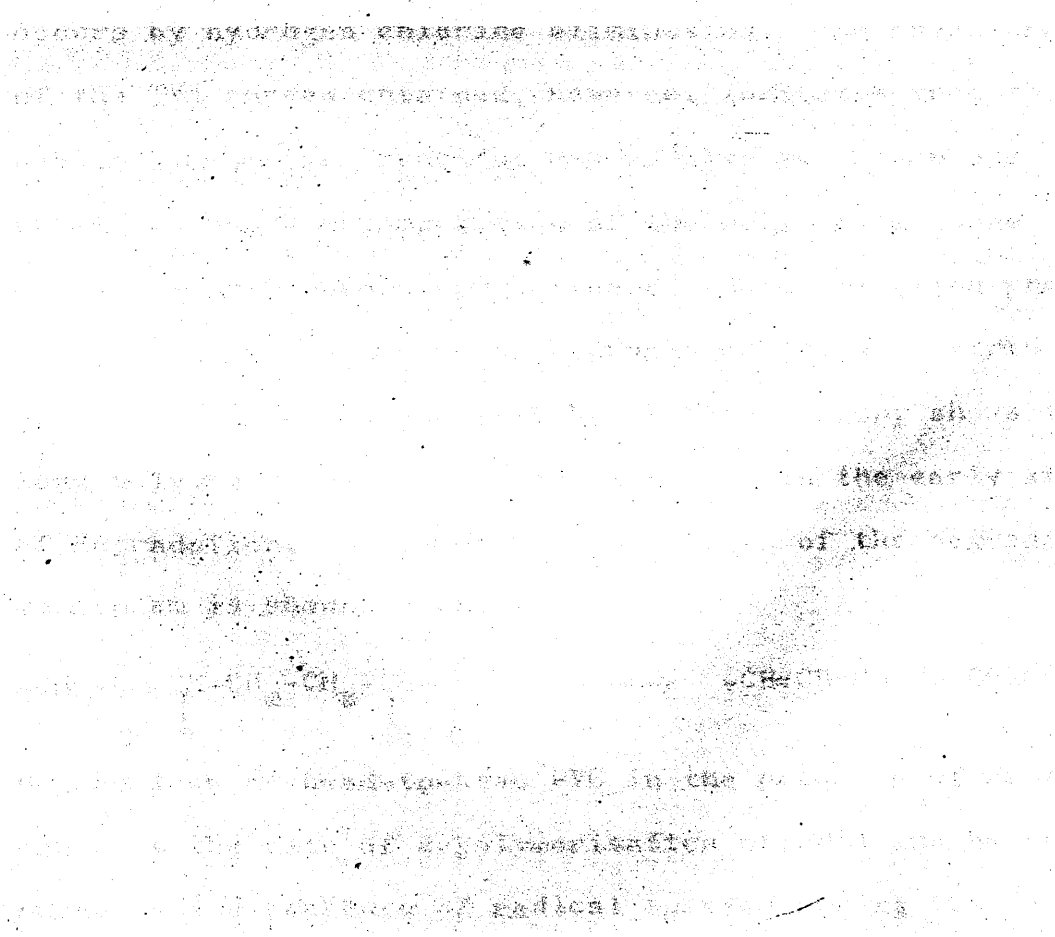
Hence, head-to-head PVBr degraded in the presence of PMMA can either enhance or curtail early monomer production. Although previous workers have reported curtailment of monomer production in blends with head-to-tail PVBr, their studies were restricted to low molecular weight PMMA[102]. As yet, no thermal data is available on blends of head-to-

Fig 50



DC-TVA curves for simultaneous degradation of head-to-head PVBr and PMMA(low Mol. Wt.),20 mg. of each, (a)unmixed, (b)mixed, Film samples.

tail PVBr with high molecular weight PMMA. Using the same argument as in Chapter 5, it follows that the increased depolymerisation of PMMA demonstrates the presence of radical species in the degradation of head-to-head PVBr. Since the degradation behaviour of head-to-head PVBr and head-to-head PVC (Chapter 5) are closely similar, it follows that the same type of degradation mechanism may be applied to both.

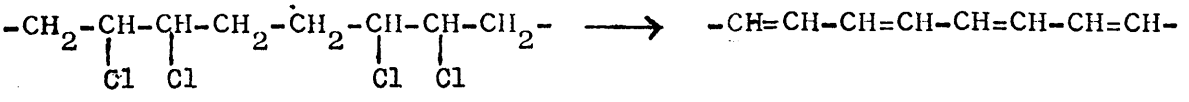


CHAPTER 7

CONCLUSIONS

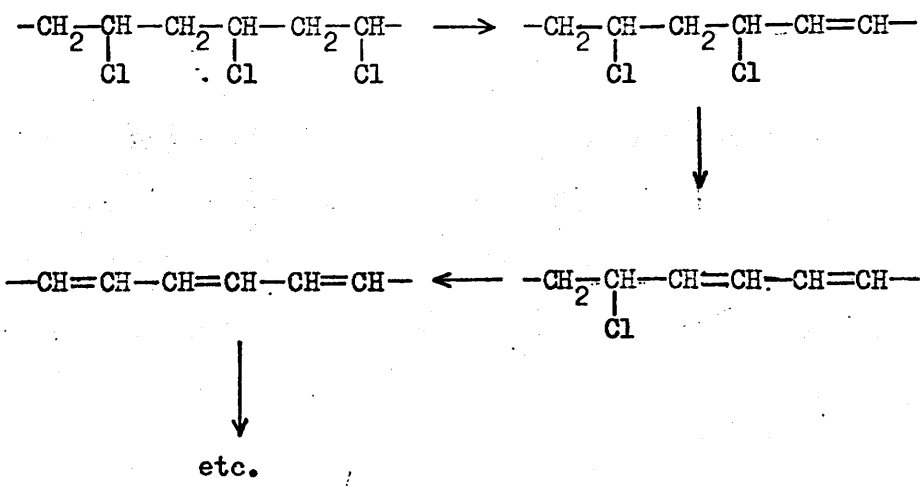
PVC having a pure head-to-head structure can be easily prepared by addition chlorination of polybutadiene. As long as the reaction is carried out in methylene chloride solution, a pure product can be isolated which has a model head-to-head structure, and can be readily classified by a variety of spectroscopic techniques.

Thermal analysis of head-to-head PVC shows that degradation occurs by hydrogen chloride elimination. The broad profile of the TVA curves obtained, however, indicates that the dehydrochlorination reaction may involve more than one stage, while secondary decomposition of the polymer backbone commences just before completion of the elimination process. Loss of polymer chlorine as hydrogen chloride is virtually quantitative, while analysis by UV spectroscopy shows that long polyene sequences are present even in the early stages of degradation. A simple representation of the degradation mechanism is shown below.

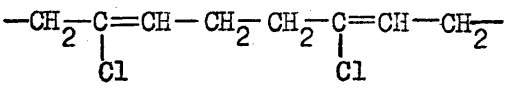


Degradation of head-to-head PVC in the presence of PMMA enhances the rate of depolymerisation of PMMA and hence suggests the presence of radical species during the degradation. To this evidence must also be added the fact that from kinetic studies of head-to-head PVC degradation,

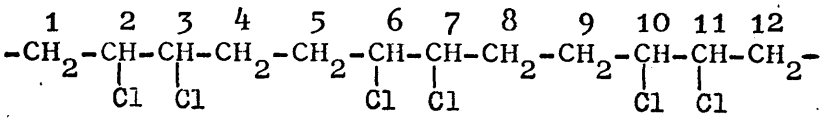
the value of n = 1.5 appeared to fit most of the kinetic data. This value has also been found for head-to-tail PVC and is typical of many radical chain reactions. However, the kinetics were treated by separating the dehydrochlorination from the other reactions which may not be a valid approach. The value of the activation energy may be used as a measure of the thermal stability, although several authors have warned[103-105] against reading mechanistic significance into the kinetic results from thermo-analytical techniques. The values 20-25 Kcals obtained from programmed and isothermal experiments are consistent with the values obtained for many radical chain reactions. Before a mechanism for the degradation of head-to-head PVC is proposed, it is worthwhile to have a brief look at head-to-tail PVC degradation. Loss of a hydrogen chloride molecule from any place in the chain, results in a chlorine atom being found allylic to the double bond. The chlorine atom is thus "activated" and loss of a hydrogen chloride molecule from the adjacent site is thereby enhanced. Hence, elimination occurs by a stepwise process.



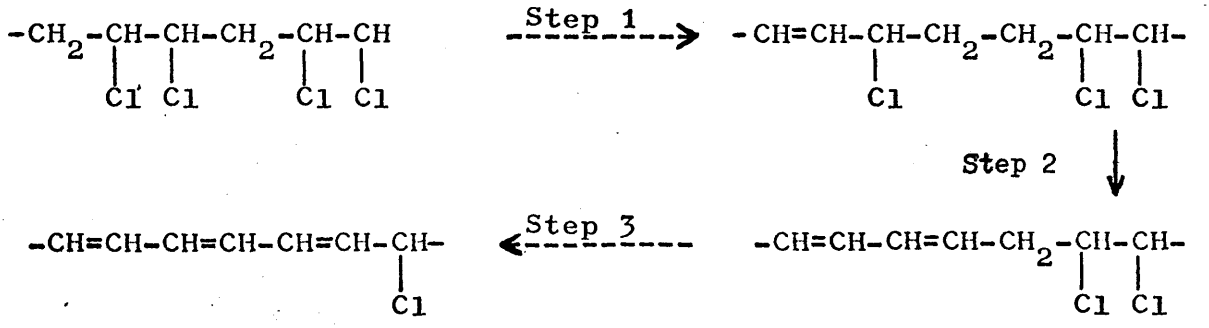
In the degradation of head-to-head PVC, Amagi and co-workers[11] have suggested the formation of isolated double bonds as shown below



However, this seems unlikely due to the strong UV spectra obtained.



To form the structure proposed by Amagi[11], hydrogen chloride has to be lost between carbon atoms 2 and 3, 6 and 7, 10 and 11, etc. In order to form a polyene sequence, hydrogen chloride has to be eliminated from carbon atoms 1 and 2, 3 and 4, 5 and 6, etc.



Hydrogen chloride elimination in Steps 1 and 2 is easily explained, however, after Step 2, only hydrogen atoms are found in allylic positions. Kinetic and polymer blend studies have, however, provided strong evidence for the presence of radical species. Hence in order to explain Step 3 in terms of radical species, the presence of hydrogen

atoms as intermediates is required. Since this seems unlikely, it is necessary to consider alternative explanations.

The portrayal of chlorinated polybutadiene as having the true head-to-head structure may be open to question. However, since a variety of techniques were used in its characterisation and since many authors have studied this polymer previously, it seems likely that its structure is that of the pure head-to-head polymer. Another possibility is that the criterion of McNeill and Neil[37,88] to justify the presence of radical species is not valid. However, without this criterion, there is no other way to explain the observed enhanced rate of depolymerisation of PMMA. The most likely solution is that the mechanism is not purely radical in nature. The broad nature of the TVA curves obtained suggests that more than one type of mechanism may hold. Hence, Step 3 in the dehydrochlorination sequence may in fact involve either or both ionic and unimolecular mechanisms. Finally, the arguments applied to head-to-head PVC, can be used when dealing with the degradation of head-to-head PVBr. The same conclusions can be reached as regards the mechanism of degradation, although since accurate UV data is unavailable, a final mechanism cannot be proposed without further study in this field.

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A P P E N D I X

Poymer Preparation

(1) Head-to-head PVC

Sample prepared by chlorination of polybutadiene in methylene chloride solution; Molecular weight (M_n) = 90,000

(2) Head-to-head PVBr

Sample prepared by bromination of polybutadiene in methylene chloride solution; Molecular weight (M_n) = 90,000

(3) PVC Breon 113

Breon 113 is a British Geon sample, stated to be free of impurities and having a molecular weight of (M_n) = 64,500

(4) Poly(methyl methacrylate)

Sample prepared by free-radical polymerisation in bulk at 60^{0}C. using azo-bis-isobutyronitrile as initiator. Conversion less than 10%. Molecular weight (M_n) = 1,400,000

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